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MINERALOGY OF THE CALCIUM PHOSPHATES IN INSULAR PHOSPHATE ROCK

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ABSTRACT

The principal constituent of insular phosphate rock is a member of the apatite series, usually a carbonate-hydroxyl-fluorine-apatite. Collophane of Sandberger (1870) and Rogers (1917, 1922) is not an amorphous species distinct from apatite. *X*-ray study of insular and continental phosphate rock, fossil bone and teeth, urinary calculi, and other materials corresponding to collophane, as defined, proves that this substance is a submicrocrystalline variety of apatite, usually carbonate-hydroxyl-apatite, or carbonate-hydroxyl-fluorine-apatite. The name collophane may conveniently be retained as a varietal designation for fine-grained, isotropic, hydrous (and often metacolloidal) types of apatite.

The original specimens of a number of ill-defined, supposed calcium-phosphate species, described by Shepard, Julien, and others, were re-examined by *x*-ray and optical methods. Ornithite of Julien (1865) is an oriented pseudomorph of carbonate-hydroxyl-apatite after crystals of brushite. Nauruite of Elschner (1913) is identical with carbonate-hydroxyl-fluorine-apatite. The names pyroguanite of Shepard (1856) and sombrerite of Phipson (1862) were applied loosely to ordinary phosphate rock and entirely lack species validity. Type specimens of pyroclasite of Shepard (1856) and of monite of Shepard (1882) were not available, but these materials are doubtless identical with apatite; non-type but probably authentic specimens of both minerals were identical with carbonate-hydroxyl-fluorine-apatite. Metabrushite of Julien (1865) and stoffertite of Klein (1901) are identical with brushite. The vague material called epiglaubite by Shepard (1856) is not entitled to further record and probably is identical with brushite. Glaubapatite of Shepard (1856) is a mixture of monetite and apatite.

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Zeugite of Julien (1865), pyrophosphorite of Shepard, Jr. (1878), martinite of Kloos (1888), and whitlockite of Frondel (1941), all are identical with artificial β-$Ca_3(PO_4)_2$. The name whitlockite is reserved for the species. Five localities are now known for this mineral, four in insular phosphate deposits and one in granite pegmatite. The material from three of the insular occurrences is a carbonate-whitlockite, analogous to carbonate-apatite, and has relatively low indices of refraction. β-$Ca_3(PO_4)_2$ definitely forms in nature from water solutions at low temperatures, although all attempts to form the substance artificially have yielded only hydroxyl-apatite. The so-called martinite of Richards (1928) from Ascension Island, South Atlantic, is monetite, and the fourth known occurrence of monetite is noted from Los Monges Islands, West Indies.

INTRODUCTION

The insular phosphate rock deposits owe their origin to the replacement of coral limestone and dolomite by phosphatic solutions derived from the leaching of superficial deposits of guano. The word guano is the Spanish rendering of the Peruvian word *huano*, or excrement, and the material represents the accumulation in favorable places of the droppings of marine birds. The mineralogy of guano itself is complex and but little known. The principal constituents are calcium phosphates, ammonium phosphate and ammonium acid phosphate, together with uric acid, sodium acid urate, ammonium and calcium oxalates, ammonium and alkali sulfates and sulfate-oxalates, guanine, xanthine, and other organic substances. Mineralogically, the underlying, derived deposits of phosphate rock are simple, and consist in bulk of members of the apatite-series.

The principal concern of this investigation has been the true identity of a number of ill-defined calcium phosphates found in insular phosphate rocks and described years ago by A. A. Julien (1840–1919), C. U. Shepard (1804–1886) and his son C. U. Shepard, Jr., and others. The speculative nature of most of these substances long has been apparent, but the descriptions still remain to burden and, in some instances, confuse later workers. In addition, an x-ray and optical study was made of phosphate rock proper and of the rather loosely defined substance termed collophane. Every effort was made to obtain the original analyzed specimens of the minerals concerned.

The writer wishes to express his appreciation to Mr. E. P. Henderson of the U. S. National Museum for making available type material contained in that part of the Shepard collection there preserved, and for loaning other specimens from the Canfield and Roebling collections. Professor Paul F. Kerr kindly permitted the examination of type specimens of minerals described by A. A. Julien and now contained in the collection of Columbia University. Further authentic study material was obtained from the Brush collection of Yale University through the courtesy of Dr. George Switzer, and from the collections of Harvard University.

APATITE

X-ray studies by Hendricks *et al.* (1931), Bredig *et al.* (1932, 1933), Royer (1939), and others, in conjunction with chemical analyses, have shown that the principal constituent of both insular and continental phosphate rock deposits is a material which falls into a rather definite range of the apatite series. The precise mineralogical definition of the material depends on the ratio of CO_2:OH:F:Cl, found by chemical analysis. No general usage has been reached, however, for the arbitrary varietal designations to be given to particular ranges of isomorphous substitution between OH-F-Cl, and C-Ca-P. The bulk of the insular apatite is a carbonate-hydroxyl-fluorine-apatite which falls approximately in the varietal range loosely assigned to francolite. Other material appears to have little or no fluorine and is properly classed as a carbonate-hydroxyl-apatite (dahllite). CO_2 is almost always present in considerable amounts as an essential constituent, but sometimes appears to be lacking. Cl always appears to be absent or present only in insignificant amounts, and a straight hydroxyl-apatite has not yet been reported from insular deposits. A hydrated tricalcium phosphate or hydrato-apatite, $Ca_9(H_2O)_2(PO_4)_6$, was considered by Hendricks *et al.* (1931) to be an important constituent of the phosphate rock from Curaçao, Dutch West Indies. The substance was thought to be distinguished among the apatite-like compounds by giving the *x*-ray pattern of β-$Ca_3(PO_4)_2$ on heating to 900°, but this behavior has since been found to be shown by ordinary hydroxyl-apatite if all of the water is driven off by heating. Bulk analyses of the Curaçao rock show several per cent of CO_2, and specimens of the substance itself give a test for CO_2, so that the material is to be properly classed as a carbonate-hydroxyl-apatite. The mineral barrandite, $(Al, Fe)PO_4 \cdot 2H_2O$, has been shown by McConnell (1940) to be an important constituent of phosphate deposits on the Island of Gran Roque, Venezuela. Barrandite and the possibly distinct mineral redondite, probably are widespread in small amounts in insular phosphate deposits, especially those in which aluminous rocks are replaced. The only other calcium phosphates now known definitely to occur in phosphate rock are brushite, monetite, and whitlockite, and these are very rare.

The apatite of the insular deposits ordinarily appears in the hand specimen as layered or banded masses of a white, yellowish or brown color. Oolitic structures and dense, compact or pulverulent varieties are less common. Pseudomorphous structures after coral or other organic remains are not infrequent. Internally banded, stalactitic or stalagmatic masses also occur. The mineral is translucent to opaque *en masse* and is transparent in thin grains. The luster is subresinous to horn-like. The color, luster and transparency may vary widely in successive bands. Under the microscope the material usually is quite isotropic. Weak anomalous birefringence is sometimes observed, and this may vary in degree from layer to layer in a single specimen. The extinction may be undulose or parallel and perpendicular to the direction of layering. Spherulitic structures also occur. The index of refraction is, on the whole, considerably less than the mean index of macro-crystalline apatite, and varies widely. The over-all range of the writer's measurements is from about 1.565 to 1.635, or somewhat greater; the ordinary range is from 1.590 to 1.625. These values are very similar to those found by Rogers (1924) for the isotropic carbonate-hydroxyl-fluorine-apatite, which comprises fossil bone. Rogers observed an over-all range of 1.573 to 1.623 with about half of 250 measurements falling between 1.600 and 1.610. The isotropic carbonate-hydroxyl-apatite which occurs in urinary calculi (Frondel and Prien (1942)) has a somewhat lower range of index, from 1.520 to 1.605, and the average index is only about 1.575. This material, however, differs from the apatite of phosphate rock and fossil bone in lacking fluorine and in containing a relatively large amount of non-essential water. The isotropic character is due to aggregate polarization in a mass composed of submicroscopic crystallites. The low and variable index reflects the large and variable content of non-essential water. Variations in index accompanying isomorphous chemical changes apparently are completely obscured by the extraneous water.

BRUSHITE

The well-established species brushite, $CaHPO_4 \cdot 2H_2O$, was first described by Moore (1865), who found the mineral in druses in phosphate rock from Aves Island in the Gulf of Maracaibo in the Caribbean Sea. The structure was analyzed by Hill and Hendricks (1936), who pointed out its isostructural relation to gypsum and who also determined optical and x-ray powder diffraction data. More recently, Terpstra (1937) has reviewed the morphology in the light of the structural relation to gypsum. Brushite is rather widespread in very small amounts in both insular and continental phosphate rock deposits. It typically occurs as drusy crystals in crevices in massive apatite and is a late-formed, low-temperature product. The compound $CaHPO_4$, monetite, forms at higher temperatures. The mineral has been observed altered to carbonate-hydroxyl-apatite (see ornithite), to quercylite (=carbonate-apatite; dahllite) and to whitlockite, β–$Ca_3(PO_4)_2$ (see zeugite). Brushite frequently occurs as an incrustation upon ancient human and animal bones and has been observed in human urinary calculi.

COLLOPHANE

The name collophane (kollophan) was originally given by Sandberger in 1870 to a layered, opal-like, "amorphous" material found in the phosphate deposits on the Island of Sombrero in the West Indies. Sombrero is located at N 18°35′, W 63°28′, about 60 miles from St. Thomas in the Virgin Islands. The original analysis is cited below.

CaO	MgO	P_2O_5	CO_2	H_2O at 100°	H_2O at ign.	Total
50.70	0.80	39.10	3.96	3.36	1.66	99.58

Sandberger deducted the CO_2 in the belief that calcite was present as an impurity and derived the formula $Ca_3(PO_4)_2 \cdot H_2O$. Lacroix (1910) and Rogers (1922) later rightly maintained that the CO_2 was an essential constituent. A number of specimens from Sombrero, variously labeled as collophane, sombrerite, or phosphate rock, which answered perfectly both to the original description of collophane and to the later use of the term as applied by Rogers, were available for study. These specimens without exception gave the *x*-ray powder pattern of hydroxyl-fluor-apatite. The original collophane thus appears to have been a member of the apatite series. If Sandberger's analysis is accepted at its face value, the mineral is a carbonate-hydroxyl-apatite (dahllite). Fluorine may have been overlooked in this analysis.

More recently, Rogers (1922, 1924) has expressed the belief that Sandberger's mineral, together with a similar material which constitutes the bulk of so-called fossil bone and phosphate rock, could not be properly classed as apatite, as had sometimes been done, but constituted a separate mineral with properties sufficiently characteristic to entitle it to recognition as a distinct species. The name collophane was proposed for the species. The criteria offered in support of the species rank of collophane, and for its distinction from apatite, may be summarized as follows. First, the substance was thought to be amorphous and not crystalline. Second, the specific gravity and the index of refraction were too low for apatite. Finally, the material always contained an appreciable amount of water, which was lacking in apatite. At that time Rogers (1914) did not consider that (OH) ever was an essential constituent of members of the apatite group, a view now known to be in error. Chemically, collophane was regarded as an amorphous "solid solution" of calcium carbonate, calcium fluoride, calcium sulfate and calcium oxide in tricalcium phosphate.

The idea is implicit in this and in later writings of Rogers, that the so-regarded amorphous minerals which approach in composition coarsely crystalline equivalents—the "homoisochemites" of Cornu, from whom the idea stemmed—should be made distinct species. Collophane thus was viewed as the amorphous equivalent of dahllite (or, better, francolite). This belief, and the designation of collophane itself as a distinct species, probably would not have been entertained if x-ray diffraction methods had been available at the time. It is now known through x-ray studies, in every instance with which the writer is familiar, that the so-regarded amorphous species in Cornu's homoisochemic pairs is merely a fine-grained crystalline aggregate of its macrocrystalline analogue. In some instances the "amorphous" species is definitely crystalline, but different from its macrocrystalline analogue; for example, chrysocolla and dioptase.

The writer in connection with this and other studies has had occasion to examine by x-ray and optical methods a large number of substances which fall into Rogers' definition of collophane. Included here were 30 urinary calculi composed of an isotropic hydrous and carbonated calcium phosphate (Frondel and Prien (1942)), samples of recent and fossil bone and teeth, phosphatized fossil wood, powdery "leached guano," and many samples of insular and continental phosphate rock. All of these substances gave distinct x-ray powder patterns of apatite and, when chemical analyses were available, could be identified as specific members of the apatite series. This also has been the experience of investigators concerned with living teeth and bone. The substance nauruite (which see), which Rogers stated to be the best and most typical form of collophane which it was his privilege to see, gives an excellent x-ray powder pattern of apatite and is identified as a carbonate-hydroxyl-fluor member of the apatite series (francolite). Collophane consists of a submicroscopic aggregate of crystallites of apatite, to which the isotropic character is due, and contains essential (OH) together with an indefinite amount of adsorbed and capillary water. The low and variable index and the low specific gravity are due to the content of non-essential water. Collophane is not a distinct species but is structurally identical with apatite. The name can conveniently be used as a varietal designation for fine-grained metacolloidal apatite.

EPIGLAUBITE

The name epiglaubite was given by Shepard (1856) to an unanalyzed mineral found in phosphate rock from Mong's Island (Los Monges) in the Caribbean Sea. The mineral was stated to occur as aggregates, or interleaved masses of minute semi-transparent crystals of a shining vitreous luster implanted upon druses of "glaubapatite." The substance was stated to consist largely of hydrous calcium phosphate, possibly also with magnesia and soda. Dana (1892) suggested with reason that the substance might be metabrushite (=brushite). Authentic specimens of epiglaubite do not appear to be extant. A non-type specimen reputedly of epiglaubite from Mong's Island was available for examination and proved to consist entirely of fine-grained dolomite. The complete inadequacy of the original description is sufficient reason for discrediting this supposed species. For purposes of record, the name may be entered questionably as a synonym of brushite.

Glaubapatite

The name glaubapatite was given by Shepard (1856) to a supposed sulfate-phosphate of sodium and calcium from a locality given as Mong's Island in the Caribbean Sea. The proper locality designation is Los Monges [The Monks, *Port.*], a collection of keys at the entrance to the Gulf of Maracaibo, Venezuela. In a later note, Shepard (1882) admitted analytical errors in the first description and withdrew the name. The mineral itself was then ascribed to pyroclasite, a substance (which see) thought by Shepard to be possibly a mixture of monetite and monite (=apatite). A non-type specimen labeled glaubapatite and answering the original description was available from the Canfield collection of the National Museum. The specimen consisted of botryoidal monetite with white, earthy whitlockite overlying massive banded apatite and limestone. The name glaubapatite is best disposed of by placing it questionably in the synonomy of both monetite and apatite.

Martinite

Martinite was described by Kloos in 1888 as a new calcium phosphate from phosphate rock deposits at St. Barbara on Table Mt., on the south coast of the Island of Curaçao, Dutch West Indies. Under the microscope the mineral is described as sharp rhombohedrons [the crystals appear as flattened rhomboids], about 0.05–0.06 mm. in size, with plane angles of 75° and 105°. The extinction is parallel to the diagonals of the rhomboids, and it is stated that there is a distinct cleavage parallel to the edges of the plates. The writer's observations on these crystals and on similar crystals from Sombrero (zeugite), however, show that the supposed cleavage is only a closely repeated zonal growth. Two chemical analyses by Kloos are cited in numbers 1 and 2, below. F was shown to be absent. A part of the water was stated to be driven off only at an elevated temperature. A recent analysis cited in Hendricks, Hill, Jacob and Jefferson (1931) is given in number 3.

	CaO	MgO	P_2O_5	H_2O	Organic	ign.	insol.	Rem.	Total
1.	46.78		47.67	4.52	0.75		0.20		99.92
2.	47.63		47.87	5.46					100.96
3.	44.58	3.28	38.42			5.43		5.74	97.45

Rem. in anal. 3 is CO_2 1.54, SO_3 0.98, Na_2O 1.86, K_2O 0.62, SiO_2 0.47, Fe_2O_3 0.27.

Two non-type specimens of martinite from Curaçao which answered the original description in every particular were available for study. One of these specimens has been analyzed and examined by x-rays by Hendricks, *et al.* (1931); the other specimen comprised the material studied optically by Larsen (1921). The x-ray powder pattern of the material from Curaçao is identical in all regards with that of whitlockite, β-$Ca_3(PO_4)_2$. Hendricks, *et al.* (1931) stated that martinite gives an x-ray powder pattern like that of $Ca_3(PO_4)_2$, but did not consider the identity of the two substances to be definitely proven. Under the microscope the mineral appears as flattened rhomboidal plates (rhombohedra) with plane angles of 75° and 105°, and otherwise is as described by Kloos. These angles would belong to a rhombohedron with a ρ angle of 63°42′, and this corresponds to the ρ angle 63°58′ of the rhombohedron $\{01\bar{1}2\}$, which determines the principal habit of the whitlockite from granite pegmatite.

Several significant differences exist between martinite and whitlockite. Martinite has $\omega = 1.607$, $\epsilon = 1.604$, which compares to the values $\omega = 1.629$, $\epsilon = 1.626$ of type whitlockite. Larsen's (1921) interpretation of martinite, as probably monoclinic, is in error; he gives $Y = 1.605$, but the value 0.02 given for the birefringence probably is a misprint for 0.002. The indices of martinite vary slightly in successive zones in the crystal, and in the outermost zone are above the values given. Anomalous birefringence effects of both an hourglass and a zonal type are sometimes observed. Spherulitic growths of a more highly birefringent mineral with an index above 1.61, are present. Chemically, martinite differs principally in containing about 4.5 per cent water. It is a question as to how much of this water is essential, especially in view of the reported presence of 0.75 per cent organic matter. Pure grains of the mineral effervesce in warm HCl. Martinite is similar to zeugite (= whitlockite) in its low indices, in its seeming water content, and in the presence of CO_2, but differs from pyrophosphorite (= whitlockite) which is identical with type whitlockite in all respects. The problem of the constitution of these minerals is discussed further under whitlockite.

The so-called martinite from Ascension Island in the South Atlantic, described by Richards (1928), proved on x-ray and optical study of the analyzed sample to be a mixture of monetite with small amounts of apatite and newberyite. The confusion with martinite arose both from the misprint for the birefringence of that species and from the fact that the optical data given for monetite at that time by Larsen (1921) are in error, and refer instead to gypsum.

METABRUSHITE

Metabrushite was described by Julien (1865) from the island of Sombrero in the West Indies. An analysis by Julien lead to the formula $CaHPO_4 \cdot 1\frac{1}{2}H_2O$, which differs only slightly from that of brushite, $CaHPO_4 \cdot 2H_2O$. The crystallographic, physical, and pyrognostic properties also are very similar to those of brushite. Crystal measurements with a contact goniometer by J. D. Dana, quoted by Julien in the original paper, showed the mineral to be monoclinic with a perfect cleavage {010}. Dana pointed out similarities in interfacial angles and cleavage with brushite. Lacroix (1897) and others have maintained that the two species were identical. A type specimen of Julien's was available for study. The poor quality of the crystals precluded morphological measurements, but the optical properties and the *x*-ray powder pattern were the same as those of brushite and the identity of the two species must be accepted.

It may be noted that Hill and Hendricks (1936) found that fine-grained brushite spontaneously loses H_2O on standing, although not when coarsely crystallized, and the writer found that a powdered commercial "C. P." preparation of $CaHPO_4 \cdot 2H_2O$ had almost entirely dehydrated in the stock bottle to monetite, $CaHPO_4$. A number of different hydrates of $CaHPO_4$ have been reported, but these are said to be variable mixtures of $CaHPO_4$ and $CaHPO_4 \cdot 2H_2O$. The observations of Bassett (1907, 1917) indicate that a compound with the supposed composition of metabrushite, $CaHPO_4 \cdot 1\frac{1}{2}H_2O$, does not exist. Julien thus appears to have analyzed a partly dehydrated sample of brushite.

MONETITE

Monetite, $CaHPO_4$, was first described by C. U. Shepard in 1882, who found the mineral in phosphate rock deposits on the islands of Moneta and Mona in the West Indies. The chemical and morphological descriptions (the latter by E. S. Dana, quoted in Shepard) leave no doubt of the species validity of the mineral. The crystallography of the natural mineral has since been shown to be identical with that of artificial crystals of $CaHPO_4$. The optical data of Larsen (1921) apparently refer to gypsum, but the later data of Barth and Berman (1934) are close to the data of Hill and Hendricks (1936) for artificial $CaHPO_4$. A type specimen of monetite from Moneta was obtained from the collection of C. U. Shepard, Sr., in the custody of the National Museum. *X*-ray powder and optical study of this material proved its complete identity with artificial $CaHPO_4$, as described by Hill and Hendricks (1936). During the course of the present studies two new localities of monetite were found. The mineral occurs in phosphate crusts on Ascension Island, in the South Atlantic, where it is associated with apatite and newberyite; this occurrence was described by Richards (1928) as martinite (which see). Monetite also occurs as botryoidal crusts, associated with whitlockite, deposited upon massive phosphate rock on Los Monges Islands in the Caribbean Sea off the coast of Venezuela.

MONITE

Monite was named by Shepard (1882) from its occurrence on the Island of Mona, located in the Caribbean Sea about 40 miles from the port of Mayaguez, Puerto Rico. Found with monetite and gypsum as snow-white, slightly coherent and impalpable masses with an earthy fracture and a dull luster. The analysis by Shepard is cited below after deducting 4.64 per cent gypsum, and recalculating to 100 per cent.

CaO	P_2O_5	H_2O	Total
51.15	41.92	6.93	100.00

A search for type specimens of this mineral was unsuccessful. Several non-type specimens were, however, available for study. These all proved on optical and *x*-ray study to be identical with carbonate-hydroxyl-apatite. Strunz (1939) also has found that the so-called monite from the Island of Mona, is apatite, but his specimens, too, doubtlessly were not of type material. The material examined by the writer comprised hard brownish crusts with a subresinous luster and did not answer the physical description of the original monite. The statement that monite melts on heating cannot be reconciled with the behavior of either whitlockite or apatite, but this effect may have been due to fluxing by admixed gypsum or monetite. The mineral may be considered to be probably identical with carbonate-hydroxyl-apatite. Dana placed monite under collophane in the sixth edition of the *System*.

NAURUITE

The name nauruite was given by Elschner (1913) to an oolitic or banded, agate-like, phosphate rock from the Island of Nauru in the Marshall Islands, Pacific Ocean. The material is brown in color, is often translucent in quite large fragments and has a resinous luster. A specimen presented by Elschner, through R. A. Daly to Harvard University, was available for study. The material gives a good *x*-ray pattern of apatite. An analysis of the Nauru phosphate, cited by Elschner, is given below.

CaO	MgO	$(Fe, Al)_2O_3$	P_2O_5	CO_2	F	SO_3	H_2O	ign. loss	Less O=F	Total
52.47	0.21	0.53	38.75	1.88	1.60	0.22	1.70	3.30	0.67	99.65

The material effervesces weakly in dilute HCl. Rogers (1922) states that material from Elschner examined by him contained about 5 per cent CO_2. Nauruite is strictly identified by the *x*-ray and the chemical data as a carbonate-hydroxyl-fluor-apatite (francolite), and is entitled neither to the name nauruite nor to the name collophane (which see), as applied by Rogers.

ORNITHITE

Ornithite is a name given by Julien (1865) to small monoclinic crystals found lining cavities in coral limestone and phosphate rock on the Island of Sombrero in the West Indies. The crystals themselves are rough and not measurable but resemble brushite. Many of the crystals have ragged terminations and other characteristics which give them much the appearance of pseudomorphs. There is a good cleavage {010}, with traces of two other cleavages. An analysis by Julien gave:

CaO	MgO	$(Fe, Al)_2O_3$	P_2O_5	H_2O+organ.	Total
45.768	tr.	4.623	40.139	9.449	99.979

Of the total water, 3.918 per cent is lost below 250° C. and 5.154 per cent is lost on strong ignition.

One of Julien's type specimens was available for study. Optical examination, together with study by *x*-ray powder and rotation methods, proved this substance to be a pseudomorph consisting of carbonate-hydroxyl-apatite. The cleavage of the mineral is a parting inherited from the perfect {010} cleavage of brushite. *X*-ray rotation photographs taken about lath-like parting fragments gave the powder pattern of apatite, but with an additional definite semblance of layer lines due to local variations in intensity along individual powder reflections.The calculated period is 6.8 ± 0.1 Å, which corresponds to the value 6.88 Å for [0001] of apatite. The crystals are interpreted as composed of crystallites of apatite, which have a tendency for preferential orientation of their [0001] axes parallel to the direction of elongation of the original brushite crystals. Pseudomorphs of hydroxyl-apatite after brushite have been formed artificially by Bassett (1917) and others. Crushed fragments appear under the microscope as optically homogeneous laths with parallel extinction. $\omega = 1.625$, $\epsilon = 1.623$. The indices and the birefringence may be low due to the presence of adsorbed and capillary water in a mass composed of subparallel crystallites. The substance gives a weak test for CO_2 and probably is correctly classed as a carbonate-hydroxyl-apatite, although determinations of F and Cl are lacking.

PYROCLASITE

Pyroclasite was originally described by Shepard (1856) from Mong's

Island (Los Monges) in the Caribbean Sea. Shepard stated the substance to consist of not far from 80 per cent of phosphate of lime and ten per cent of water, with the remainder made up of carbonate of lime, sulfate of soda, a little insoluble matter and traces of sodium and fluorine. The material did not give a CO_2 test but definitely contained F. In a later note, Shepard (1882) described a second occurrence of pyroclasite from the Islands of Mona and Moneta. The mean of two analyses cited by Shepard is given below.

CaO	Fe, Al phosph.	SO_3	P_2O_5	H_2O, ign. loss	insol.	Total
40.125	2.900	6.825	39.080	10.335	0.885	100.120

Shepard deducted 20.847 per cent of extraneous matter, mostly gypsum, from this analysis and derived the formula $6CaHPO_4 \cdot Ca_3P_2O_2 \cdot H_2O$. Shepard entertained some doubt as to the species validity of the mineral, however, and thought that the substance might be only a mechanical mixture of monetite and monite—a very probable explanation (see glaubapatite). Specimens of pyroclasite from neither Mong's Island, nor Mona and Moneta could be found in the Shepard collection. A specimen labeled pyroclasite from Jarvis Island, West Indies, was, however, available for study. The specimen consisted of massive red oolitic apatite with small open cavities lined with a crust of a creamy white, small botryoidal mineral with a greasy luster. The latter material gave the x-ray pattern of apatite and effervesced in dilute HCl. The physical properties and chemical composition of the original pyroclasite from Los Monges leave little doubt but that this mineral is a member of the apatite series, perhaps a hydroxyl-fluorine-apatite.

PYROGUANITE

Pyroguanite is a name given by Shepard (1856) to the ordinary phosphate rock from Mong's Island (Los Monges) in the Caribbean Sea off the Gulf of Maracaibo. The substance was thought to have been guano thoroughly fused by the action of trap rock, and to consist of two species, pyroclasite and glaubapatite (which see). Shepard's notion of the origin of the material was gained from Captain A. F. Winslow of the sailing ship *Jane Dolen*. Winslow's ship had been forced by storm into the port of Charleston, South Carolina, in 1856, where Shepard examined its cargo of rock phosphate.

PYROPHOSPHORITE

The name pyrophosphorite was given by C. U. Shepard, Jr., in 1878, to a supposed anhydrous calcium pyrophosphate found in phosphate rock from an unnamed locality in the West Indies. Two closely agreeing chemical analyses were given, and their mean is cited below.

CaO	MgO	$(Fe, Al)_2O_3$	P_2O_5	SO_3	SiO_2	ign. loss	Total
44.462	3.090	0.437	50.799	0.628	0.367	0.390	100.173

Specimens of snow-white, earthy pyrophosphorite from the collection of C. U. Shepard, Sr., were available for study. *X*-ray powder photographs of the mineral were identical in every respect with those of whitlockite, β-$Ca_3(PO_4)_2$. The mean index was 1.625 ± 0.003, and the birefringence was estimated at about 0.003. These data agree closely with those for whitlockite ($\omega = 1.629$, $\epsilon = 1.626$). The substance was not entirely homogeneous but contained several per cent, at least, of an unidentified mineral with indices below 1.62. Samples of the material effervesced in spots when treated with acid, but this appears to be due only to admixture. The question of the variation in the apparent water content and in the indices of refraction of pyrophosphorite, zeugite, and martinite, all of which are identical with whitlockite, is discussed further under whitlockite.

SOMBRERITE

The name sombrerite was proposed by Phipson (1862) for a substance composed largely of tricalcium phosphate found as rock masses on the Island of Sombrero in the West Indies. Phipson's account of the material and later remarks by Julien (1863) leave no doubt that the description refers not to a specific mineral species but to the ordinary phosphate rock, *en masse*, mined at the locality. Specimens labeled sombrerite from Sombrero were found in several collections. These proved on optical and *x*-ray study to be apatite.

STOFFERTITE

Stoffertite is a name given provisionally by Klein (1901) to a mineral from the phosphate rock deposits on the Island of Mona in the West Indies. The morphological and optical properties agree exactly with those of brushite, but stoffertite was thought to differ from this species in having a slightly higher water content. This is very scant evidence for proposing a new species. It may be noted that hydrates other than $CaHPO_4 \cdot 2H_2O$ have not been found (cf. Bassett (1907, 1917) and de Schulten (1903)) in the system $CaHPO_4$-H_2O. Specimens of stoffertite were not available for examination. The mineral, however, is probably identical with brushite.

WHITLOCKITE

Whitlockite, β-$Ca_3(PO_4)$, was originally described by the writer in 1941. The mineral was found as large rhombohedral crystals as a hydrothermal product in a granite pegmatite at the Palermo quarry, North Groton, New Hampshire. Whitlockite is identical with the low temperature polymorph of artificial anhydrous tricalcium phosphate, β-$Ca_3(PO_4)_2$, described by Trömel (1932) and others. The optical data for β-$Ca_3(PO_4)_2$ given by Schneiderhöhn (Trömel (1932)) are cited in Table 2. Photographs of the x-ray powder pattern are given by Trömel (1932), and Trömel and Möller (1932), and the spacing data by Bredig, Franck and Füldner (1932). The x-ray spacing data for analyzed crystals of the natural mineral are given in Table 1. The x-ray pattern and optical properties of the high temperature modification, α-$Ca_3(PO_4)$, differ considerably from those of the beta form. The inversion temperature is about 1180° according to Bredig, *et al.* (1932). A complete survey of the work on the basic calcium phosphates, and related systems, is given by Eisenberger, Lehrman and Turner (1940).

TABLE 1. X-RAY POWDER DIFFRACTION DATA FOR WHITLOCKITE
Analyzed crystals from North Groton, N.H. Cu radiation

d	I	d	I	d	I
8.03	2	2.25	2	1.60	1
6.55	5	2.19	2	1.55	5
5.24	8	2.16	2	1.46	1
4.07	4	2.07	1	1.43	1
3.45	7	2.04	2	1.40	1
3.35	1	2.00	1	1.38	1
3.21	9	1.93	6	1.25	2
3.02	1	1.88	5	1.24	2
2.88	10	1.82	1	1.18	1
2.75	3	1.77	3	1.15	1
2.68	1	1.72	7	1.11	3
2.60	9	1.70	1	1.09	1
2.52	2	1.67	2	1.05	1
2.41	2	1.63	1	1.03	1

In the course of the present study, zeugite of Julien (1865) from Sombrero, pyrophosphorite of Shepard (1878) from an unknown locality in the West Indies, and martinite of Kloos (1888) from Curaçao, were found to be identical with whitlockite. A fourth new occurrence of whitlockite was found in phosphate rock from Los Monges Island in the Caribbean Sea. The mineral formed soft, earthy, white to gray masses under a botryoidal crust of monetite. In these occurrences, whitlockite has formed from water solutions under essentially atmospheric conditions of temperature and pressure; in two instances the mineral occurred as pseudomorphs after hydrated minerals, brushite ($CaHPO_4 \cdot 2H_2O$) and gypsum

($CaSO_4 \cdot 2H_2O$). The natural occurrences of whitlockite are unusual in that all attempts to synthesize $Ca_3(PO_4)_2$ from water solutions have resulted in the formation of hydroxyl-apatite. Both the alpha and beta modifications of $Ca_3(PO_4)_2$ hitherto have been known only as high temperature products from dry systems.

The material from some of the occurrences in insular phosphate deposits is of special interest in that it differs from type whitlockite and artificial β-$Ca_3(PO_4)_2$ in having relatively low indices of refraction and a relatively high (Ca, Mg)O : P_2O_5 ratio, and in the presence of carbon dioxide and a considerable amount of possibly essential water. The data are summarized in Table 2.

TABLE 2. OPTICS AND COMPOSITION OF WHITLOCKITE

	β-$Ca_3(PO_4)_2$, Artificial	Whitlockite, North Groton	"Pyrophosphorite," West Indies	"Zeugite," Sombrero		"Martinite," Curaçao	Whitlockite, Los Monges
ω(Na)	1.622	1.629	1.625	1.608		1.607	1.600
ε	1.620	1.626		1.605		1.604	
CaO	54.22	46.90	44.462	44.18	44.24	46.78	
MgO		2.53	3.090	3.25	3.92		
P_2O_5	45.78	45.68	50.799	47.07	46.03	47.67	
H_2O	—	0.48	0.39	2.99[2]	2.97[2]	4.52	
CO_2	—	none	none	present		present	present
(Ca,Mg):P:O	3:2:8	2.97:2.01:8[1]	2.62:2.15:8	2.75:2.10:8	2.83:2.07:8	2.65:2.14:8	
S.G.	3.19 (calc.)	3.12	—	2.971		2.896	

[1] 1.91 per cent FeO and 1.73 per cent Fe_2O_3 as FeO have been added to the sum of the XO as given in calculating the ratio (Ca,Mg):P:O.

[2] Includes organic matter.

The divergence of the analyses from the requirements of $Ca_3(PO_4)_2$ can be ascribed to analytical error and, especially in the case of pyrophosphorite, to admixture. The role of the water reported in the analyses of the material from Sombrero and Curaçao, is quite uncertain. Part of the water, at least, is non-essential. The material from both of the localities when heated gently in a closed tube loses water, gives off an organic odor and turns a deeper shade of color. Zeugite when heated in air at 925° for one hour turned dead-white in color and lost 3.69 per cent in weight. The x-ray powder pattern of the heated material is still identical with that of whitlockite. The x-ray pattern and indices of whitlockite did not change when the mineral was heated at 930° for two hours.*

* Whitlockite exhibits a peculiar color change when cooled. The material assumes an orange-yellow color when the temperature drops below red heat, and this color gradually changes to yellow on further cooling. The material becomes pure white again when the temperature drops below *ca.* 200°. A similar behavior was found by Bassett (1917) for ig-

The whitlockite from Curaçao, Sombrero, and Los Monges gives a definite CO_2 test, as previously noted, but "pyrophosphorite" and type whitlockite from granite pegmatite does not contain CO_2. The carbonated and seemingly hydrous material is distinguished from the other material by relatively low indices of refraction (see Table 2). It has been established with some certainty, through the work of McConnell and Gruner (1937, 1940), that carbon can substitute isomorphously for Ca, P, or both, in the apatite series, with a concomitant decrease in the indices of refraction. The existence of this substitution in whitlockite must now be considered very probable. The zoning in the crystals presumably reflects variations in the Ca, P/C ratio. Zoned carbonate-apatite crystals have been described by McConnell and Gruner (1940). It is questionable whether the low indices also are connected with the presence of water, either essential or non-essential, in the crystals. Possibly (OH) substitutes for O in the PO_4 groups, but there is no increase in birefringence, nor is there reason to expect the indices to be markedly lowered thereby unless there was also an increase in cell dimensions. The x-ray photographs do not indicate any change in the dimensions of the cell. If (OH) does not enter the constitution of carbonate-whitlockite, it appears necessary for C to substitute equally for both Ca and P, in order to maintain electrical neutrality. The indices of the whitlockite from North Groton are probably slightly high as compared with pure $Ca_3(PO_4)_2$, due to the presence of iron in isomorphous substitution.

The question of the priority of the names of natural β-$Ca_3(PO_4)_2$, also arises. The name zeugite of Julien (1865) was first published, but the original description is so incomplete and, insofar as the chemical interpretation is concerned, erroneous, that the mineral could not again be recognized without a complete re-examination of the original material. None of the three later workers, who unwittingly described the same substance, was led to suspect the true nature of zeugite. As a matter of fact, Julien himself did not view the substance as a very definite species, and considered it to be an amorphous, accidental product, composed of variable proportions of a hypothetical compound, $8CaO \cdot 3P_2O_5$, for which the name was intended. The mere proposal of a name and a few non-definitive observations are not sufficient to establish and maintain a mineral species. Similar remarks apply to martinite of Kloos (1888), and especially to pyrophosphorite of Shepard (1878). The characterization of martinite was further complicated by two erroneous later descriptions.

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nited hydroxyl-apatite, who showed that it was due to the presence of traces of copper oxide and not to rare-earths. The writer also observed that ignited hydrated tricalcium phosphate (hydroxyl-apatite) prepared according to the method of Hendricks *et al.* (1931) took on a very faint lilac tint when cooled.

Often a more or less vague early name can be retained if there is any definite reason for believing that a later found substance corresponds to the original material, in order to avoid further burdening the synonomy of the science. In the present case, however, it appears proper to retain the name whitlockite for the species.

ZEUGITE

The name zeugite was given by Julien (1865) to the substance of certain porous pseudomorphs after metabrushite (=brushite) from the Island of Sombrero in the West Indies. The two analyses given by Julien are cited below. Julien considered the principal constituent of the mineral to have the composition $8CaO \cdot 3P_2O_5$ and the remainder to be due to admixture.

	CaO	MgO	$(Fe,Al)_2O_3$	P_2O_5	CO_2	SO_3	F	NaCl	H_2O+ org.	Total
1.	44.18	3.25	0.54	47.07	tr.	0.39	tr.	n.d.	3.07	98.50
2.	44.24	3.92	0.78	46.03	0.48	tr.	tr.	1.08	2.97	99.50

One of Julien's original specimens and several non-type specimens were available. *X*-ray powder photographs of the mineral were identical in every respect with that of whitlockite, β-$Ca_3(PO_4)_2$. Under the microscope the mineral corresponds in every particular to crystals of martinite. The indices are: $\omega = 1.608$, $\epsilon = 1.605$. Julien's two analyses are in rather poor agreement with the requirements for $(Ca, Mg)_3(PO_4)_2$. The phosphorus was determined by a relatively inaccurate method and may be somewhat in error. The role of the water reported in the analyses is quite uncertain; part of it without doubt is non-essential. Pure grains of the mineral give a CO_2 test with warm HCl. Zeugite is identical with martinite in its low indices, apparent water content, and in the presence of CO_2. Both substances differ from pyrophosphorite (=whitlockite) and type whitlockite in these respects. The problem of the constitution of these substances is discussed further under whitlockite. Strunz (1939) found a supposed specimen of zeugite to be identical with apatite, but his material could not have been authentic.

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LARGE AND SMALL GARNETS FROM FORT WRANGELL, ALASKA

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Abstract

Measurement of 133 garnets from Fort Wrangell, Alaska, shows conclusively that there is an excellent correlation of habit with size. These garnets all show both {110} and {211}. The larger the garnet the more prominent {110}. Numerical and graphical methods for dealing with problems of this type are explained.

Introduction

It has been pointed out that garnets on the whole conform well to the Donnay-Harker law of crystal morphology[1] which requires that the order of importance of the forms shall be: {211}, {110}, {321}, {100}, {210}, {332}, ... So far as the writer has been able to determine, all garnet crystals show either {211} or {110}, or both, and one or the other is nearly always the dominant form. The predominance of these forms over all other forms is shown by the summary in Table 1, in which are included only the records of forms on garnets whose chemical composition was at least approximately known. Unquestionably the predominance of the two principal forms is much greater than indicated in the table, for, in many cases, the very occurrence of other forms has prompted mineralogists to examine garnets more closely and to report their results.

It seems not unreasonable to suppose that a variation in the habits of garnets might be correlated with variations in composition, and Table 1 shows that such a correlation does exist. For the ugrandite group {110} is definitely the most important form, no other form being known on uvarovite. Pyrope, which is found in ultrabasic rocks, at best shows only a poor suggestion of crystal form. Hintze lists only one "pyrope" for which crystal forms are given and this was excluded from the list because it contains less than 50% of the pyrope end-member. On almandite the two principal forms occur with about equal frequency. Almandite is mostly a constituent of crystalline schists, but some garnets in granitic and related rocks are also essentially almandite. Further distinctions on the basis of paragenesis might permit a finer correlation; for instance, garnets in glaucophane schist are always dodecahedrons.[2] The garnets listed as spessartite in the table include a few igneous and pegmatite garnets in which the spessartite end-member amounts to less than 50%,

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[1] Donnay, J. D. H., and Harker, D., A new law of crystal morphology extending the law of Bravais: *Am. Mineral.*, **22** (Palache number), 446–467 (1937).

[2] Pabst, A., The garnets in the glaucophane schists of California: *Am. Mineral.*, **16**, 327–333 (1931).

TABLE 1. SUMMARY OF GARNET HABITS

		{211}	{211} {110}	{110} {211}	{110}	Other combinations	
8 Uvarovites							
	K				1		
	H				6		
	P				1		
	sum				8		
80 Grossularites							
	K	2	2	3	1	4	33%
	H	4	—	13	7	25	51%
	P	1	1	3	10	4	21%
	sum	7	3	19	18	33	42%
75 Andradites							
	K	1	1	2	3	4	36%
	H	6	1	14	11	15	32%
	P	2	—	2	11	2	12%
	sum	9	2	18	25	21	28%
Pyrope							
		Commonly in anhedral grains					
90 Almandites							
	K	6	4	2	4	—	—
	H	13	9	10	11	5	10%
	P	4	2	4	12	4	15%
	sum	23	15	16	27	9	10%
40 Spessartites							
	K	1	—	—	—	—	—
	H	2	2	2	2	1	11%
	P	14	5	4	3	4	13%
	sum	17	7	6	5	5	12%
293 Garnets		56	27	59	83	68	23%

K, recorded by Kokscharow in Materialien zur Mineralogie Russlands (**1858**).
H, cited by Hintze in Handbuch der Mineralogie (**1897**).
P, recorded in literature since 1897.

for instance, the Ely, Nevada, rhyolite garnet.[3] On spessartites, {211} definitely predominates and thus they show the best agreement with the Donnay-Harker law in this respect.

That garnet composition may be a controlling factor is suggested by the only two syntheses of garnet crystals, recently cited by Donnay.[4] Andradite has been synthesized in dodecahedrons[5] and spessartite in trapezohedrons,[6] the same forms which are dominant, respectively, on natural crystals of these varieties.

Table 1 also shows that combinations involving other forms besides {211} and {110} have been most frequently found on grossularite and andradite. From Table 2 it may be seen that these varieties also show the greatest number of forms. The reason is doubtless that these varieties, being mostly contact garnets, often found in calcareous rocks or vuggy situations, have a better opportunity for a rich development of forms. Hintze records that "the implanted crystals are comparatively richer in forms than the enclosed crystals," but does not point out that this gives rise to a correlation of composition with the richness in forms. Records for garnets lend no support to the view of "small crystals having a richer variety of faces which are less representative of conditions of growth."[7]

The forms are listed in Table 2 in order of their rank according to the Donnay-Harker law. The first seven forms in the list show frequencies in accord with this law, except for a slight preponderance of {110} over {211}. One cannot expect any correspondence for the remaining forms, most of which are very rare.

Though the most conspicuous anomalies with respect to the Donnay-Harker law are restricted to uvarovites and garnets in glaucophane schists, and though other correlations of habit with composition or paragenesis can be traced, this is no explanation of the departures from the law. There is no doubt but that all garnets belong to the space group *Ia3d* and they might all be expected to show the same order of importance of forms.

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[3] Pabst, A., Garnets from vesicles in rhyolite near Ely, Nevada: *Am. Mineral.*, **23**, 101–103 (1938).

[4] Donnay, J. D. H., and Faessler, Carl., Trisoctahedral garnet from the Black Lake Region, Quebec: *Univ. Toronto Studies, Geol. Series*, **46**, 19–24 (1941).

[5] Michel, L., Sur la reproduction du grenat melanite et du sphene: *Bull. soc. franç. mineral.*, **15**, 254–257 (1892).

[6] Gorgeu, A., Sur la production artificielle de la spessartine: *Bull. soc. franç. mineral.*, **6**, 283–284 (1883).

[7] Buerger, M. J., The law of complication: *Am. Mineral.*, **21**, 702–714 (1936).

TABLE 2. FORMS RECORDED ON GARNETS OF KNOWN CHARACTER

	Rank after D-H	Grossularite				Andradite				Almandite				Spessartite				All
		K	H	P	Sum	K	H	P	Sum	K	H	P	Sum	K	H	P	Sum	
{211}	1	10	38	9	57	6	36	6	48	11	37	12	60	1	7	27	35	200
{110}	2	9	44	18	71	9	39	15	63	10	32	21	63	—	7	17	24	221
{321}	3	3	13	2	18	—	3	—	3	—	2	3	5	—	1	2	3	29
{100}	4	1	12	2	15	—	7	—	7	—	3	—	3	—	—	1	1	26
{210}	5	—	8	—	8	2	5	—	7	—	—	1	1	—	1	2	3	19
{332}	6	—	5	1	6	—	3	2	5	—	—	—	—	—	1	1	2	13
{431}	7	—	3	—	3	—	3	—	3	—	—	1	1	—	—	—	—	7
{310}	11	—	—	—	—	—	1	—	1	—	—	—	—	—	—	—	—	1
{541}	12	—	1	—	1	—	—	—	—	—	—	—	—	—	—	—	—	1
{111}	14	1	4	—	5	—	1	—	1	—	—	2	2	—	—	—	—	8
{320}	16	—	2	—	2	—	2	—	2	—	—	—	—	—	—	—	—	4
{432}		—	—	—	—	—	1	—	1	—	—	—	—	—	—	—	—	1
{520}		—	—	—	—	—	1	—	1	—	—	—	—	—	—	—	—	1
{433}		—	—	—	—	—	—	—	—	—	1	—	1	—	—	—	—	1
{530}		—	—	—	—	—	1	—	1	—	—	—	—	—	—	—	—	1
{221}		—	1	—	1	—	1	—	1	—	1	—	1	—	—	—	—	3
{610}		—	—	1	1	—	1	—	1	—	—	—	—	—	—	—	—	2
{540}		—	1	—	1	—	—	—	—	—	—	—	—	—	—	—	—	1
{311}		—	—	1	1	—	1	—	1	—	—	—	—	—	—	—	—	2
{322}		—	1	—	1	—	—	—	—	—	—	—	—	—	—	—	—	1
{331}		—	1	—	1	—	—	—	—	—	—	—	—	—	—	—	—	1
{511}		—	—	—	—	—	1	—	1	—	—	—	—	—	—	—	—	1
{533}		—	—	—	—	—	1	—	1	—	—	—	—	—	—	—	—	1
{722}		—	—	—	—	—	1	—	1	—	—	—	—	—	—	—	—	1
{744}		—	—	—	—	—	1	—	1	—	—	—	—	—	—	—	—	1
Number of forms					16				20				9				6	25

K—columns, summary of forms recorded by Kokscharow in Materialien zur Mineralogie Russlands (1858).

H—columns, summary of forms cited by Hintze in Handbuch der Mineralogie (1897).

P—columns, summary of forms recorded in the literature since 1897.

DESCRIPTION OF MATERIAL

The excellent garnet crystals occurring in great abundance in the crystalline schist near the mouth of the Stikine River, not far from Fort Wrangell, Alaska, have found their way into most mineral collections. Sometime ago the writer noticed that crystals from this locality show a curious correlation of size and habit. With the encouragement of Dr. Donnay, he decided to make a quantitative study of this correlation in the hope that it may throw some light on certain factors affecting habit.

Through the courtesy of Dr. W. F. Foshag, 120 loose crystals and one matrix specimen were borrowed from the United States National Museum for study. This material was supplemented by 15 loose crystals and numerous matrix specimens in the collections of the University of California. All but two of the loose crystals were suitable for measurement.

The occurrence of these garnets has been repeatedly described.[8] They are disseminated through certain beds in schist lying close to intrusive quartz diorite. Buddington[9] now regards them as "probably dynamothermal metamorphic." The crystals measured, and those usually described, are one to three centimeters in diameter, but a large slab in the collections of the University of California is studded on one side with similar garnets only a millimeter or two in diameter. The garnet crystals are very easily separated from the groundmass which consists largely of quartz and mica. As far as could be determined the rock contains no garnet other than the prominent porphyroblasts under discussion.

All of the larger crystals show {211} and {110}. No other forms were seen and none have been reported. Vicinal development is not conspicuous. Striations on both forms, where present, are in the {111} zone. According to Kalb,[10] who ignored the Law of Bravais in his speculation, such garnets belong to Niggli's dodecahedral type and are "minerogenetically older."

All the garnets are deep red and they show little if any variation in color. They are generally fractured but not altered. A thin section through the center of a large crystal shows no birefringence, color, or alteration, and not even a trace of zoning. The crystal shows numerous minute inclusions of quartz. These are arranged in lines and groups by sectors as if governed by garnet growth.

COMPOSITION AND PROPERTIES

An analysis of these garnets by A. F. Kountze was published long ago[11] together with a brief description. With it appears a crystal drawing that corresponds closely to the appearance of the largest of these crystals.

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[8] Wright, F. E., and Wright, C. W., The Ketchikan and Wrangell Mining Districts, Alaska: *U. S. Geol. Sur., Bull.* **347** (1908).

Buddington, A. F., Mineral deposits of the Wrangell District: *U. S. Geol. Sur., Bull.* **739,** 51–75 (1923).

Buddington, A. F., and Chapin, Theodore, Geology and mineral deposits of Southeastern Alaska: *U. S. Geol. Sur., Bull.* **800** (1929).

[9] Personal communication, August 12, 1941.

[10] Kalb, G., Vizinalerscheinungen auf den Hauptflächen isoharmonischer Kristallarten: *Zeits. Krist.*, **75,** 311–322 (1930).

[11] Dana, E. S., System of Mineralogy, 6th ed., 442 (**1892**) the last of the "almandite" analyses.

TABLE 3

SiO_2	39.29%	$RO:Al_2O_3:SiO_2$
Al_2O_3	21.70	2.89: 1.00:3.18
Fe_2O_3	*tr.*	
FeO	30.82	Al=69.6
MnO	1.51	Sp= 3.5
MgO	5.26	Py=21.2
CaO	1.99	Gr= 5.7
	100.57	

The calculation of the end-members is slightly at variance with that of Ford,[12] as is also the determination of the indices given below, but it is in agreement with the end-member composition given by Eskola.[13]

The properties given in Table 4 were all determined on the crystal represented by the spot farthest to the right in Figs. 3 and 4.

TABLE 4

	Calculated[14]	Observed
Lattice constant	11.50Å	11.50±0.01Å
Specific gravity	4.12	4.10
Refractive index	1.797	1.806

The agreement is such as to leave little doubt but that the garnet examined has approximately the composition reported by Kountze for garnets from this locality. The lattice constant was determined from 23 alpha lines on a powder pattern kindly prepared by Mr. W. H. Dore. The specific gravity was determined on the Berman balance. The refractive index was interpolated for the *D* line from measurements on two prisms by the minimum deviation method, using a mercury arc for illumination. They gave the values:—

6234Å	5780Å	5461Å	4358Å	4046A
1.8025	1.8071	1.8102	1.8261	1.836

To check the uniformity of composition of the garnet, two prisms with angles of about 50° were cut from a large crystal in such a way that the prism edge was a line running from the surface approximately through the center. The indices of refraction were determined at various points along these prisms. No variations exceeding the limits of error were found. The specific gravity of large garnets, small garnets, and chips is nearly the same. This, together with the thin-section observations, indicates that these garnets vary little, if at all, in composition.

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[12] Ford, E. W., A study of the relation existing between the chemical, optical and other physical properties of the members of the garnet group: *Am. Jour. Sci.*, **40**, 33–49 (1915).

[13] Eskola, P., On the eclogites of Norway: *Videns. Skrifter*, 1. No. **8**, Christiania (1921).

[14] For a garnet of the composition given in Table 3, from the properties of end-members given by M. Fleischer, The relation between chemical composition and physical properties in the garnet group: *Am. Mineral.*, **22**, 751–759 (1937).

MEASUREMENTS

133 crystals were measured in order to establish the correlation of habit and size among the Fort Wrangell garnets. The crystals were selected solely to cover the maximum range of sizes conveniently measurable and without regard to the habit displayed.

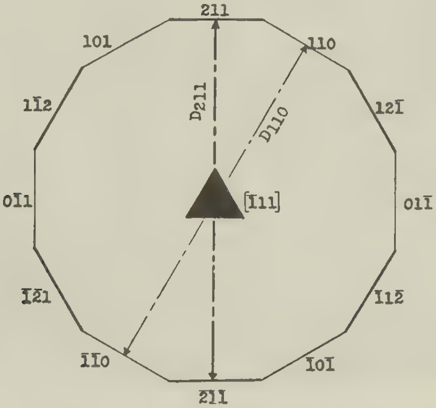


FIG. 1. Cross-section through a garnet crystal normal to a trigonal axis.

The manner in which the garnets were measured may be seen from Fig. 1. Any isometric crystal has 4 trigonal (or hexagonal) zones. The faces of both forms present on these garnets lie in these zones, each (110) face lying in two such zones. The relative sizes of the faces of several forms on a crystal are connected in a simple way with the distances between opposite like faces. The smaller this distance for a given form, relative to the distance for other forms on the same crystal, the larger the faces of the given form. The relations in the present case may easily be seen from Fig. 1. When the distances between opposite faces, $D_{\{110\}}$ and $D_{\{211\}}$, are alike the widths of the faces of both forms are the same. Let $D_{\{110\}}$ and $D_{\{211\}}$ be the mean values of all the D_{110}'s and all the D_{211}'s, respectively, for a given crystal. Let $D_{\{110\}}/D_{\{211\}}$ be called the habit ratio, H. The faces of $\{110\}$ will get relatively narrower as H increases, and vice versa. The limiting values $2/\sqrt{3}$ and $\sqrt{3}/2$, or 1.155 and 0.866, represent the ratios at which $\{110\}$ and $\{211\}$, respectively, disappear. For all crystals showing faces of both forms this ratio must lie between these limiting values. In this way a numerical expression can be given to the habit variation of these garnets. A sample calculation is shown in Table 5.

TABLE 5. MEASUREMENTS OF A GARNET FROM FORT WRANGELL, ALASKA, TO ESTABLISH HABIT AND MALFORMATION

D_{110} $D_{\{110\}}$	$\lvert D_{\{110\}}-D_{110}\rvert$	D_{211} $D_{\{211\}}$	$\lvert D_{\{211\}}-D_{211}\rvert$
1.71 cm.	0.007 cm.	1.64 cm.	0.088 cm.
		1.71	0.018
1.71	0.007	1.82	0.092
		1.69	0.038
1.73	0.027	1.79	0.062
		1.67	0.058
1.75	0.047	1.74	0.012
		1.62	0.108
1.65	0.053	1.79	0.062
		1.75	0.022
1.67	0.033	1.76	0.032
		1.76	0.032
Mean 1.703	Mean 0.029	Mean 1.728	Mean 0.052

Habit: $H=\frac{1.703}{1.728}=0.985.$

Malformation: $M_{\{110\}}=\frac{0.029}{1.703}\times 100=1.64,$ $M_{\{211\}}=\frac{0.052}{1.728}\times 100=3.00.$

Measurements of distances between opposite faces were made to 0.1 mm. with vernier calipers. From duplicate measurements of half a dozen crystals it was concluded that the average error of H, determined in this way, is well under one per cent.

HABIT VARIATION

The habit variation of these garnets is well exhibited in Fig. 2, which shows that the habit differences of large and small garnets are not connected with any difference in environment. As stated above, there seems to be no compositional variation of the garnets to which the habit differences might be attributed.

The correlation of habit with size can be shown by plotting the habit ratio, H, against $D_{\{211\}}$. This is done in Fig. 3, on which are plotted the values for all 133 garnets measured. The correlation is very good and the distribution of the 14 points representing the "UC specimens" shows that measurement of this small number would have sufficed to indicate the trend.

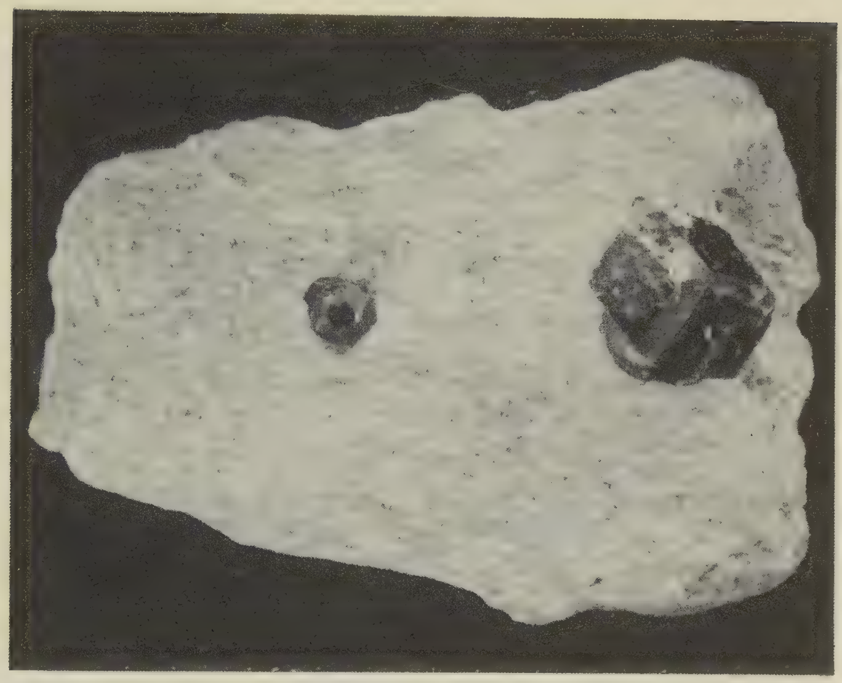


FIG. 2. Two garnets in matrix from Fort Wrangell, Alaska, illustrating variation of habit. Natural size. Specimen lent by the United States National Museum.

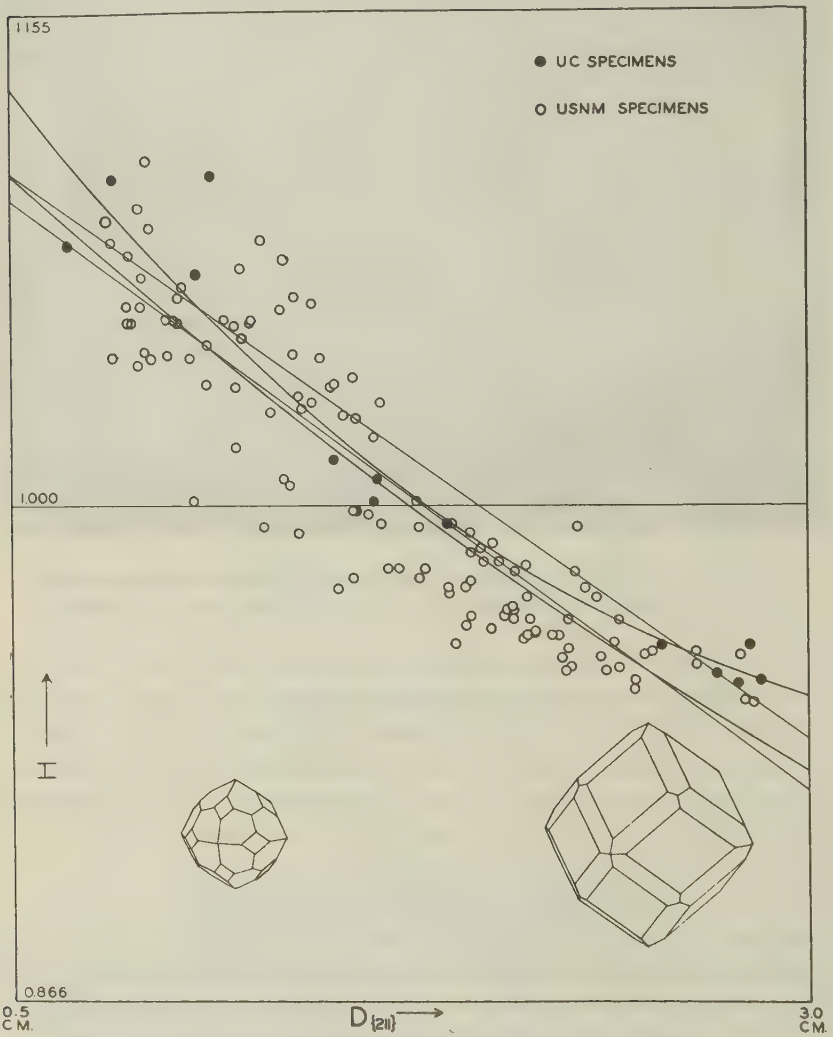
The mean value of H for the UC specimens is 1.008. The equations:—

$$H = 1.1395 - 0.07109\, D_{\{211\}}, \text{ and}$$
$$H = 1.196 - 0.143\, D_{\{211\}} + 0.0192 (D_{\{211\}})^2,$$

calculated by least squares, represent the trend for the UC specimens and determine the upper line and curve, respectively, in Fig. 3. The mean value of H for all specimens is 1.0063. The equations:—

$$H = 1.1336 - 0.0746\, D_{\{211\}}, \text{ and}$$
$$H = 1.1509 - 0.0968\, D_{\{211\}} + 0.00635 (D_{\{211\}})^2,$$

calculated in a similar manner, represent the trend for all specimens and determine the lower line and curve, respectively in Fig. 3. An extrapolation is best made from the last equation. Since the first constant is just under the limiting value of H at which {110} disappears, it indicates that very small garnets belonging to this group would still show traces of that form. This is borne out by observation. It was not feasible to make caliper measurements on these very small specimens, but of 15 crystals between 1 and 2 mm. in diameter, examined under a binocular microscope, each showed {211} as the dominant form and some faces of {110}, corresponding to a habit ratio just under 1.155. On these small crystals the (110) faces are very bright and show no vicinal development, whereas the (211) faces are not so bright and are roughly striated parallel to [111].



HABIT VARIATION OF FORT WRANGELL GARNETS

FIG. 3

Extrapolation from the curve based on UC specimens alone would have indicated that garnets under about 3 mm. in diameter would show only {211}. This is not in accord with observations and, of course, the lower curve based on all of the data is a better representation of the trend.

Extrapolating towards the larger values of D one may calculate that, if the trend in the measured range continues, the crystals would show the dodecahedron only when $D_{\{110\}}$ exceeds 3.5 cms.

It may seem arbitrary to handle the data in the manner shown in Fig. 3. One might, for instance, plot H against $D_{\{110\}}$. This gives much the same sort of diagram, as is shown by the equations:—

$$H = 1.1549 - 0.0805\, D_{\{110\}}, \text{ and}$$
$$H = 1.2249 - 0.1685\, D_{\{110\}} + 0.0240(D_{\{110\}})^2,$$

corresponding to the line and curve, respectively, indicating the trend for the 14 UC specimens in such a diagram. The constants in these equations are quite similar to those for the corresponding equations for $D_{\{211\}}$.

MALFORMATION

Table 5 also shows how a measure of the malformation, M, may be obtained from the measurement of distances between opposite like faces on each crystal. For instance, the ratio of the average difference, $|D_{\{211\}} - D_{211}|$, to $D_{\{211\}}$ times one hundred, may be thought of as the percentage of malformation, $M_{\{211\}}$. On an ideal crystal the values of D_{211} would be the same for all parallel pairs of faces, the departure from the mean would be zero and the malformation zero. This sort of measurement can be made independently for each form, or combined for all forms.

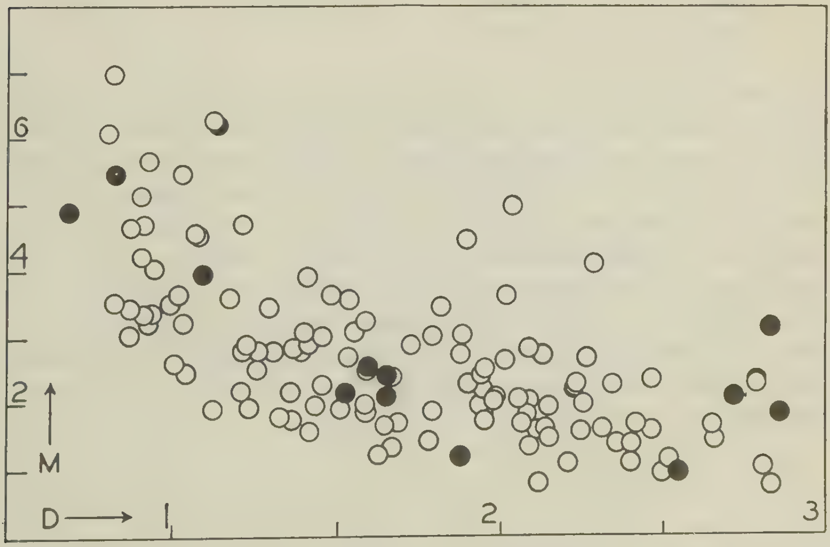


FIG. 4. Malformation of {211} on garnets from Fort Wrangell, Alaska. Open circles—USNM specimens, solid circles—UC specimens.

on a crystal. No additional measurements beyond those previously described are needed.

As noted by several earlier observers, the malformation of these crystals is very slight. Figure 4 shows the malformation of {211} plotted against the diameter. The correlation is not quite so good as for the habit variation, but there is a definite decrease in malformation with increase in size.

A graph similar to Fig. 4 is obtained if $M_{\{110\}}$ is plotted against $D_{\{110\}}$. Since the malformation of {110} is, on the average, considerably less than that of {211}, its variation with size is not as pronounced, but the trend is the same. {110} also tends to show less malformation on the larger crystals.

Since error in the caliper measurements might make a contribution to M and since this contribution would vary inversely with the dimensions, one might suspect that the correlation seen in Fig. 4 is due largely to this cause. To check this point the five smallest of the UC specimens were remeasured after an interval of half a year with the following results:—

H		$M_{\{211\}}$	
First measurement	Remeasurement	First measurement	Remeasurement
1.014	1.021	2.15	2.36
1.072	1.067	3.96	3.74
1.103	1.110	6.22	6.08
1.102	1.100	5.45	5.62
1.081	1.082	4.90	4.45

The near duplication of the original results shows that, at the worst, the error of measurement makes but a slight contribution to M and does not affect the correlation of malformation with size in any important degree.

A further check on these relations may be obtained from the distribution of M with respect to H, shown in Table 6. Comparison of columns 1 and 2 in this table leaves no doubt that {110}, as well as {211}, tends to show greater malformation when H is greater than unity, that is, on the smaller crystals. The table also shows clearly that {211} tends to be more malformed than {110}, regardless of the value of H, but this tendency is slightly stronger on those garnets on which it is the more prominent form.

Table 6. Correlation of Malformation with Habit

		$H>1$	$H<1$	All
	Number of garnets	61	72	133
	Percentage of total	46%	54%	
	Average $M_{\{211\}}$	3.41	2.16	2.73
	Average $M_{\{110\}}$	2.48	1.80	2.11
$M_{\{110\}} < M_{\{211\}}$	Number of garnets	47	49	96
	Percentage of group	77%	68%	
	Percentage of total			72%
	Average $M_{\{211\}}$	3.73	2.24	2.97
	Average $M_{\{110\}}$	2.41	1.53	1.96
$M_{\{110\}} > M_{\{211\}}$	Number of garnets	14	23	37
	Percentage of group	23%	32%	
	Percentage of total			28%
	Average $M_{\{211\}}$	2.33	2.01	2.13
	Average $M_{\{110\}}$	2.72	2.36	2.50

Conclusion

It seems that as they grow the shapes of these garnets tend to approach more closely to the ideal crystal forms while the departure from the Donnay-Harker law increases.

X-RAY PETROLOGY OF SOME FINE GRAINED FOLIATED ROCKS

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Abstract

X-ray examination of oriented thin plates of some fine grained foliated rocks (slate and shale) shows the following:

(1) A definite relation exists between the angular spread of the reflections from the oriented platy minerals and the cleavability of the rock. The smaller the spread the better is the foliation.

(2) Greater angular spread of reflections from platy minerals results when the x-radiation is parallel to the lineation than when it is perpendicular to it. No lineation was discovered by x-ray analysis which was not easily visible in the specimen concerned.

(3) Parting of shale is explained in the same manner as foliation in schists, i.e., by parallel orientation of platy minerals.

(4) Supplementary optic examination of the quartz in one of the rocks gives a typical girdle orientation of the axes, although random orientation is indicated from its x-ray photograph.

(5) The methods employed thus far permit subdivision of the platy minerals into a kaolinite-chlorite group and a muscovite-illite group (white mica). Their relative proportions can be estimated by inspection of the chief reflection rings of each group.

(6) In the slates examined, white mica>kaolinite-chlorite where cleavability is high; kaolinite-chlorite>white mica where cleavability is low.

Introduction

Fine grained foliated rocks of the slate and shale type are not only abundant in the earth's crust, but are of great economic value. Petrologic studies of these rocks are therefore important. Until recently the petrographic microscope provided the principal means of investigation, and after a half century of service it is still the standard equipment for this purpose. However, as such studies of fine grained rocks are difficult and the results often inconclusive, the advantages of a suitable x-ray method are obvious. This paper explores a special technique and indicates ways in which further work may be undertaken. Although not the first report of its kind dealing with fine grained foliated rocks (1, 2, 3, 4), some advances in technique are outlined and conclusions offered which may prove of value.

Methods

Two types of data can be obtained from x-ray examination of mixed crystal aggregates—one compositional, the other structural. These may be obtained independently, or, as described below, in one operation. If the sample of rock is powdered in order to identify its components, obviously no structural data are obtainable from the photograph. If, however, a thin oriented plate of the rock is prepared, as first carried out by Sander (3), the photograph so obtained yields both compositional and structural data. This method, well known to metallurgists, is the one followed in the present investigation. A detailed account of the preparation of specimens and the equipment used will be found in a recent publication (5). In brief, a thin plate of the rock, ground to a thickness of .02–.04 mm., is mounted on gummed paper tape (*Sp* in Fig. 11) and placed in the path of an *x*-ray beam. This beam is reduced to a diameter of .5 mm. by a suitable collimator. The reflected radiation gives patterns on the film of the type illustrated in Figs. 1 to 8. A scanning device (Fig. 12) systematically moves the specimen to and fro in its own plane, without rotation, thus permitting the radiation to encounter a much larger number of grains than would be possible with a stationary specimen. With unfiltered radiation from a copper target the average time of exposure is 4 hours at 45 KV and 10 MA, using Eastman No-Screen *x*-ray film and Kodalk developer. This latest procedure has three advantages over that previously used: (1) thinner rock plates and faster film reduce exposure time very considerably, (2) a smaller collimator opening gives much better definition of the orientation pattern, and (3) translatory movement of the specimen (scanning) gives cleaner pictures and permits use of relatively coarse grained material.

Results of Investigation

The material selected for presentation in this paper illustrates a number of common structural and compositional features of fine grained foliated rocks. Enough accessory material was studied so that unusual characteristics could be eliminated. For this reason it was not thought necessary to include full petrographic descriptions of the rocks analyzed in Figs. 1 to 8.

All the specimens were sectioned perpendicular to the foliation. The foliation is perpendicular to each figure, with east-west orientation as shown in Fig. 13. Two features of these photographs are at once striking. One is the conspicuous, unbroken, outer ring; the other is the discontinuity of the inner rings. It can be shown by use of the Bragg equation that the unbroken outer ring is composed of reflections from rhombohedral planes of quartz. The photograph of powdered quartz in Fig. 10 provides direct evidence, showing in addition two smaller rings identifiable also in most of the rock photographs. It can likewise be shown that the discontinuous inner rings are composed of reflections from the basal planes of platy minerals such as muscovite or kaolinite.[1] The important point is that randomly oriented grains yield continuous rings, and systematically oriented grains broken rings.

A third feature, conspicuous in Figs. 1 to 4, is the spotted appearance of 1 and 3, compared with 2 and 4. The majority of the spots lie on the three quartz rings. The two photographs having this selective speckling were produced from stationary specimens, whereas Figs. 2 and 4 are from scanned specimens of the same rocks. In neither pair of photographs is there any speckling of the inner rings. The inference is that the grain size of the quartz is greater than that of the associated platy minerals. The latter do not require scanning to yield smooth rings, enough grains being encountered within the .5 mm. x-ray beam to give smooth ring segments. This conclusion is confirmed by optical study.

Figures 2 and 4 are photographs of two Vermont slates, the former a greenish-gray rock with inferior cleavage, the latter a brick-red material possessing excellent splitting properties. This contrast in cleavability is due to the varying degree of parallelism of the platy minerals in the two slates. Figure 2 shows wide ring sectors for these minerals, whereas Fig. 4 shows very narrow segments. The unoriented quartz in the two rocks plays no known role. Good foliation is indicated in Figs. 5 and 6 of a crenulated black phyllite from Nova Scotia and in Fig. 7 of a black roofing slate (locality unknown). Figure 8, on the contrary, is from a shale in which the degree of parallelism of platy minerals is relatively poor. In these and other examples studied, the excellence of the cleavage is shown by the size of ring sector in which the reflections are concentrated. By measuring the approximate angle of the ring sectors an index of cleavability could be established which might have use in commercial work. (See also Sander(3).)

The Vermont specimens (Figs. 1 to 4) show no lineation, and series of thin plates cut at various angles to each other perpendicular to the foliation give identical photographs. In contrast, the crenulated slate in Figs. 5 and 6 has marked lineation, shown both megascopically and by x-ray examination. In Fig. 6 the lineation is perpendicular to the paper, whereas in Fig. 5 it is parallel to the paper and horizontal. The spread of the inner ring reflections is noticeably greater in Fig. 6 than in Fig. 5, indicating an inferior degree of parallelism of the platy minerals where the section is cut perpendicular to the lineation than in other orientations perpendicular to the lineation. This inference can be confirmed by visual examination of the rock. Sander (3) first showed this relation by *x*-ray study. It also appears, without comment, in photographs published by the author (4) in 1935.

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[1] Figure 9, of muscovite powder, does not show these inner rings. Apparently too few cleavage flakes in the powder are nearly enough parallel to the x-ray beam to produce the strong, low-order reflections typical of the foliated rocks. Attempts to reproduce these reflections by mixing the flakes with glass powder failed. The single conspicuous ring in Fig. 9 is referable to 006 and coincides fortuitously with the strong quartz ring of Fig. 10.

The preceding paragraphs are concerned with structural features of the investigation alone. Additional and important information regarding the kinds and proportions of platy minerals is also obtainable. As experience has shown the desirability of obtaining basal plane reflections in work with platy minerals, the orientation of the specimens illustrated in Figs. 1 to 8 is thus highly favorable for identification purposes. Nagelschmidt (6) and others described a method for producing this orientation artificially in unconsolidated aggregates of clay minerals. In foliated rocks it is ready-made. Figure 13 shows, on the same scale as the photographs, the position of the chief basal plane reflections for kaolinite-chlorite (7.2Å) and muscovite-illite[2] (10Å). These correspond with the actual reflections in the photographs. No trace of reflections from other common platy minerals, such as serpentine and talc, was found. In the rocks producing photographs 1 to 8, routine optical examination fails to prove the presence or absence of chlorite. Rough heavy liquid fractionation and preliminary *x*-ray examination failed on the other hand to disclose any kaolinite. In consequence, therefore, reflections referable to $d_{(001)}=7.2$Å cannot as yet be allocated. Fractionation by a supercentrifuge and thermal analysis of the products (8) will probably be necessary to decide the issue. This holds also for the white micas, muscovite and illite, which have not as yet been properly identified. The platy minerals in the rocks can be discussed, therefore, only in general terms, and only one subdivision is possible at present.

Kaolinite and chlorite on the one hand, and white mica on the other, each produce one strong basal reflection which may be used to compare relative proportions of mixtures of the two. Thus Fig. 2 shows that kaolinite-chlorite > white mica (slate with poor cleavage), whereas Fig. 4 shows that white mica > kaolinite-chlorite (slate with excellent cleavage). The crenulated black slate (Figs. 5 and 6) contains almost no kaolinite-chlorite; the roofing slate (Fig. 7) indicates a predominance of white mica; the shale (Fig. 8) has approximately equal amounts of kaolinite-chlorite and white mica. A study of the weaker reflections for each of

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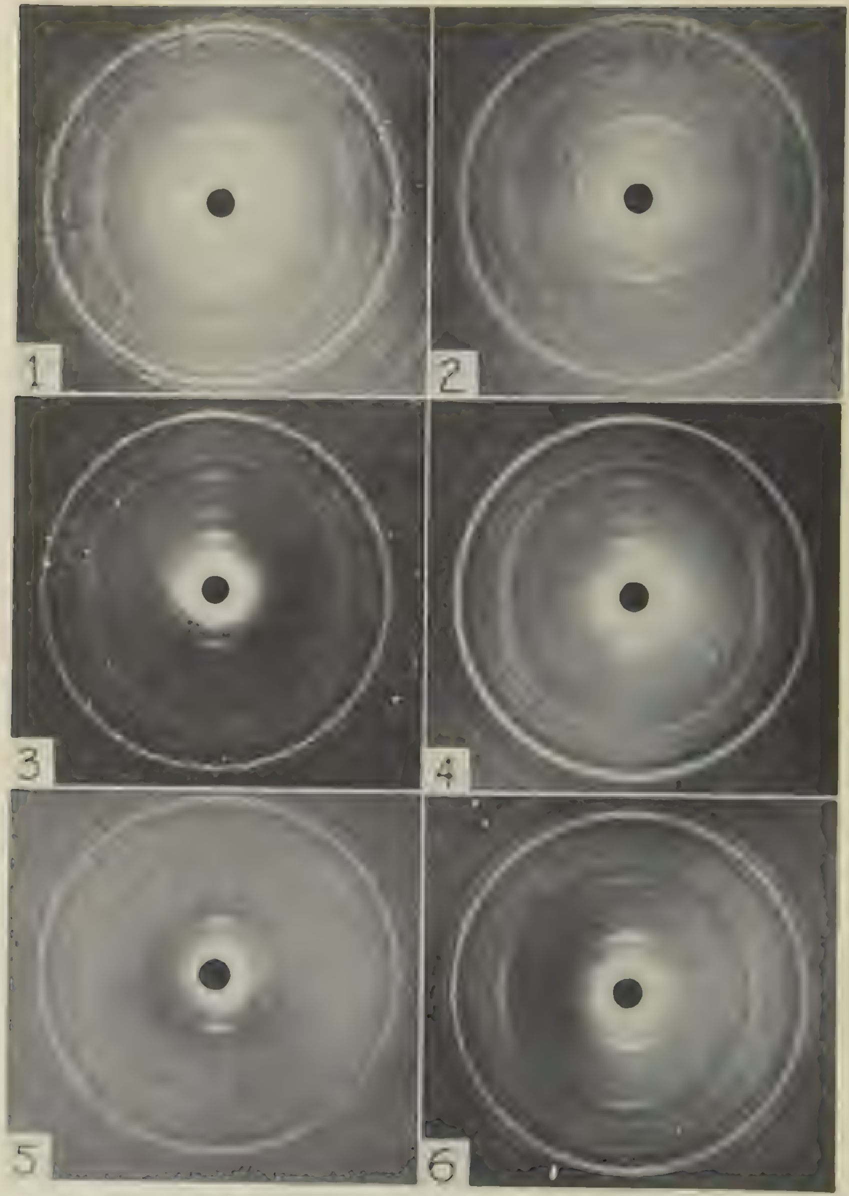
[2] Under illite is included the Al-poor white mica characteristic of clay sediments. As Grim (7) uses it, illite is a stop-gap term for white micaceous material which is definitely not muscovite. Much "sericite" is properly classified as illite, pending a more accurate determination.

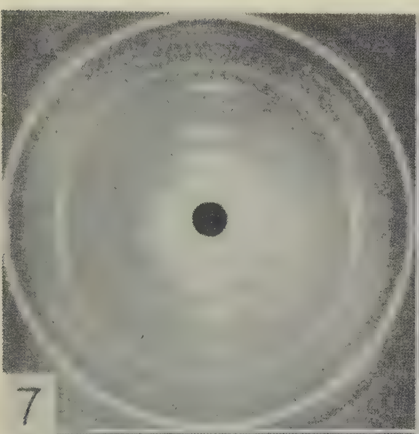


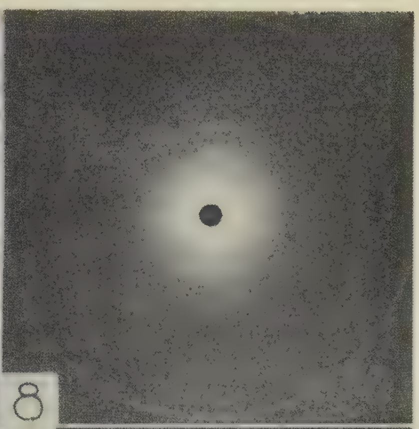
In Figs. 1 to 6 all foliation is perpendicular to the page and is horizontal. Exposure time, about 4 hours at 10 MA, 45 KV, using Eastman No-Screen x-ray film and .5 mm. collimator. Thickness of specimens, .02–.04 mm. All specimens scanned except Figs. 1 and 3.

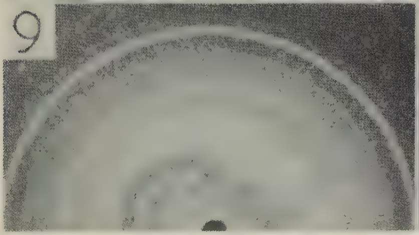
Figs. 1 and 2. Greenish-grey slate, Poultney, Vt., collected by D. M. Larrabee. Fig. 1 is unscanned.

Figs. 3 and 4. Red slate, Poultney, Vt., collected by D. M. Larrabee. Fig. 3 is unscanned.

Figs. 5 and 6. Black, crenulated slate, Montague, N. S., collected by W. H. Newhouse. Fig. 5 is parallel to the foliation; Fig. 6 is perpendicular to the foliation.







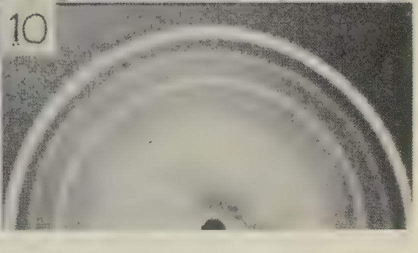


FIG. 7. Black roofing slate, locality unknown.

FIG. 8. Upper Parry shale, Kansas, collected by W. J. Mead.

FIG. 9. Powder pattern of muscovite. Note absence of reflections close to center of figure.

FIG. 10. Powder pattern of quartz.

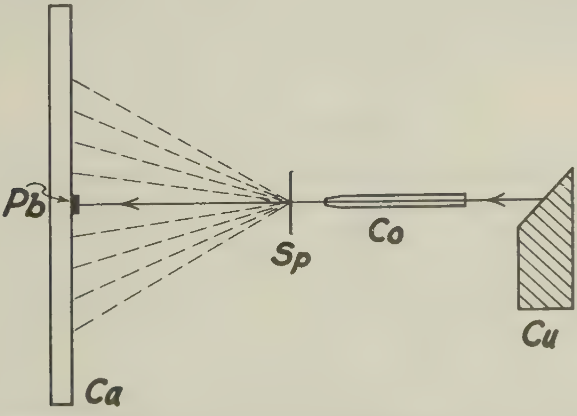


FIG. 11. Diagrammatic drawing of the essential apparatus for *x*-ray photography of thin slices of rocks. Cu—copper target, Co—collimator, Sp—rock specimen, Ca—cassette containing film, Pb—lead button. Broken lines indicate paths of assumed reflections from the specimen.

these minerals, in general, confirms these conclusions about relative proportions. By standardizing and refining the procedure it might be possible to determine a semi-quantitative mode for these constituents and for quartz. This has not been attempted.

Several additional features of the x-ray photographs may be noted. In Fig. 7, and less conspicuously in some others, a concentration of reflections to the right and left of the center is clearly seen. These originate from $(0kl)$ planes of the vertical [001] zone (prism planes and pinacoids other than the basal) of the platy minerals. No attempt has been made to assign these reflections to particular minerals or specific planes, as they are of little significance where associated 001 reflections occur.

A second minor feature is somewhat puzzling. The basal pinacoid reflections are not always equally developed above and below the centers of the photographs. This is particularly evident in Fig. 3. In Fig. 4, a scanned photograph of the same specimen, there is approximate equality. It might be assumed that the relatively few platy grains encountered by the x-radiation to produce Fig. 3 (unscanned) were not representative of the average dimensional orientation of the slate, whereas the scanning used to produce Fig. 4 neutralized such inequalities. In Fig. 7, however, derived from a scanned slate specimen, the unequal development of reflections above and below its center is marked. More study is needed to explain this point correctly.

A third, easily overlooked, characteristic of several photographs is the lack of exact alignment of the "center of gravity" of the ring sectors above and below the center. (The position of the central black spot itself has no significance in this connection.) This non-alignment is evident in Figs. 1, 2, 3, 4, and 6 and can be checked by inspection or by use of a straight-edge. No explanation of this feature is forthcoming at present.

Discussion of Results

Although desirable for clean photographs, scanning is not essential where the investigation concerns rocks as fine grained as those described here. It is necessary only where the grain size is larger than that of normal slates and shales. Indeed, to obtain evidence of the relative grain size of quartz and associated platy minerals, a stationary specimen is required (cf. Figs. 1 and 2, 3 and 4).

Estimation of the degree of cleavability in slate (see preceding section) is obvious from a study of the hand specimen, without x-ray analysis, where the contrast is as great as that shown in Figs. 1 to 4. However, for smaller variations the x-ray method is superior if not definitive, and its possible usefulness should not be discounted.

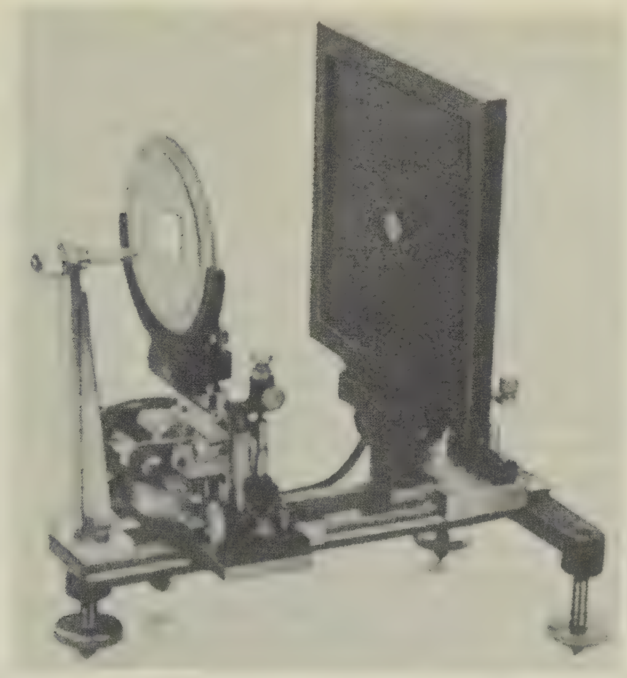
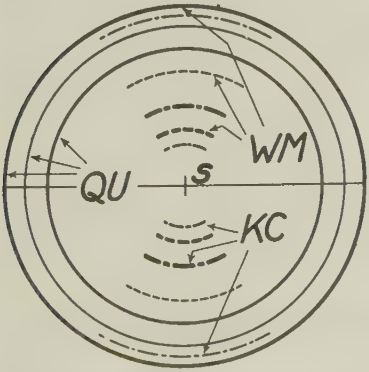


FIG. 12. Adjustable *x*-ray scanning camera. The mechanism beneath the specimen holder moves the specimen to and fro in parallel position across the path of the *x*-ray beam.



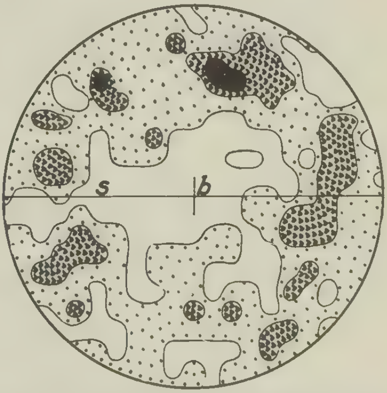


FIG. 13. Key to principal reflections observed in Figs. 1 to 8. QU—quartz, WM—muscovite and/or illite, KC—kaolinite and/or chlorite. S—trace of foliation. Intensity of reflections indicated by thickness of lines. Scale of figure same as Figs. 1 to 8.

FIG. 14. Diagram showing optic orientation of 250 quartz axes of the crenulated black slate, Montague, N. S. Figure has same orientation as Fig. 6; *s*—trace of foliation; *b*—lineation. Contours 4-3-2-1-0%.

The cleavability, or parting, of shale has been considered in some quarters as independent of parallel orientation of platy minerals, and, as petrographic proof is not easy to obtain, the problem has remained largely a matter of opinion rather than fact. Figure 8 indicates a fair degree of parallelism of the platy minerals with the parting surface of the shale. The parallelism is at least as good as that for the slate of Figs. 1 and 2, where dependence of foliation on parallelism of platy minerals is not in doubt. The evidence thus far shows that parting in shale is explained in the same way as normal foliation in other rocks.

Sander (3) was the first to study lineation by the x-ray method. Figures 5 and 6 illustrate the principle involved, as described in the preceding section. It does not seem likely, however, that the x-ray method is sensitive enough to disclose lineation not visible by inspection or optical means. The slates illustrated in Figs. 1 to 4, and in Fig. 7, without visible lineation, were studied unsuccessfully for x-ray evidence of this kind. Sander's observation, that unequal development of basal plane reflections above and below is typical of tectonites oriented as in Fig. 5 (parallel to the lineation), is not confirmed in the present study. Indeed, the opposite is true in Figs. 5 and 6. Sander assumed the inequality to be due to a "shingling" arrangement of the platy constituents, thus supporting the hypothesis that movement of material occurred in the foliation surface perpendicular to lineation. However this may be, x-ray evidence offers inconclusive support at the present time.

The random orientation of quartz[3] in these fine grained rocks, based on x-ray evidence, has already been noted. Sander (3) confirmed this by optic study, obtaining diagrams of quartz axes showing no orientation pattern. X-ray evidence, however, is not final. Optical study of the quartz in the crenulated black slate of Figs. 5 and 6 results in the orientations shown in Fig. 14, which is a common quartz pattern in schistose rocks. The failure of the x-ray method to detect quartz girdle orientation of this kind has been noted also in medium and coarse grained rocks. Unless the degree of orientation is high (as with the platy minerals in foliated rocks), optical examination is therefore necessary to complete the analysis.

The essential minerals found in these rocks—quartz, white mica, kaolinite and/or chlorite—support the earlier optical investigations of authorities such as Behre, Dale, and Renard (9) and Berg (10). There is no confirmation of the conclusions of Anderson and Chesley (2) that kyanite, and to a lesser extent corundum, are, next to quartz, the most prominent constituents of slate. They found no muscovite or kaolinite. It is improbable that kyanite or corundum would be developed under the normal temperature-pressure conditions obtaining during slate formation. If present as detrital minerals, it is still less probable that slates from widely separated localities would all show high concentrations.

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[3] The alert reader will have noted that the main quartz ring in many of the photographs is conspicuously white above and below, and in line with, the inner discontinuous rings. This is due to the superposition of 006 muscovite reflections on the main quartz ring (cf. Figs. 9 and 10) and does not indicate quartz orientation. In support of this, it will be noted that it occurs most conspicuously in those photographs showing white mica as the predominant platy mineral.

Grim and Bradley,[4] as a result of recent unpublished work on shale, find chlorite predominant over kaolinite. It is quite possible that this is true also for many slates, but, as already noted, a more thorough investigation, using the super-centrifuge and thermal analysis, will probably be required.

The relative proportions of kaolinite-chlorite and white mica have already been noted. In the slates (Figs. 1 to 7) this seems to be referable to cleavability. That is, white mica predominates where cleavage properties are well developed, and kaolinite-chlorite where cleavage is less well developed. In the single shale investigated (Fig. 8), where white mica and kaolinite-chlorite appear equally abundant, this conclusion receives neither support nor negation. Grim's study (11) of some Illinois shales shows that illite occurs instead of muscovite, and is more abundant than kaolinite. As basal plane reflections for the white micas are identical, the species of mica in the rocks under discussion is uncertain. No chemical or optical work has been undertaken in connection with this problem. Obviously, no further generalizations will be warranted until more is known of the distribution of muscovite, illite, chlorite, and kaolinite in a wide variety of fine grained foliated rocks.

ACKNOWLEDGMENTS

I am particularly indebted to D. M. Larrabee of Poultney, Vermont, for providing excellent samples of a number of Vermont slates, two of which are described in this paper. W. H. Newhouse and W. J. Mead likewise provided critical material. Acknowledgment is also made to M. J. Buerger for generous assistance with the technical aspects of x-ray photography. R. E. Grim and W. F. Bradley offered constructive criticism which has improved the paper considerably. Otto von der Heyde designed and built the camera used in the work and O. F. Tuttle prepared many of the thin rock plates.

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[4] Personal communication.

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GOLD-NICKEL MINERALIZATION AT ALISTOS, SINALOA, MEXICO

PHILIP KRIEGER* AND ARTHUR F. HAGNER†.

ABSTRACT

An occurrence of gold-nickel ore from Alistos, Mexico, is described. It consists of two types: (1) gold-niccolite, containing minor amounts of gersdorffite and maucherite; (2) gold-millerite, with associated pentlandite, gersdorffite, and violarite. The mineral assemblage, particularly the association of native gold with niccolite and primary millerite, is considered unusual. The ore is believed to have originated from solutions which produced alteration in a peridotite stock. The latter cuts surrounding flat-lying volcanics, the chief one being an enstatite latite. The mineralization responsible for the unusual group of minerals is interpreted as being hypogene.

INTRODUCTION AND ACKNOWLEDGMENTS

Several years ago an interesting suite of gold and nickel ore from the Gloria property at Alistos, Sinaloa, Mexico, was submitted to the authors for study. Work was undertaken as a joint project and was nearing completion when interrupted by Professor Krieger's unfortunately fatal accident. The junior author has completed the project and presents this study as a joint contribution, both in appreciation of the inspiration received from a former professor and friend, and as a description of a unique ore.

The mineral assemblage of the Gloria ore, particularly the association of abundant native gold with niccolite, and the presence of primary millerite, also containing gold, is extraordinary. This association, together with pentlandite and rare minerals, such as maucherite, violarite, and gersdorffite, is unusual. The occurrence of pentlandite free from associated pyrrhotite is also noteworthy.

Native gold has been but rarely observed with niccolite, and in deposits where it has been described it is commonly associated with base metal sulphides and sulpho-salts of silver. In the Gloria occurrence at Alistos, however, the metallic constituents associated with gold consist almost entirely of nickel-bearing minerals.

Field data and additional material for study were obtained from Mr. W. H. Triplett and Mr. F. L. Wingfield, of the Cia. Minera de Penõles, S. A. Grateful acknowledgment is made to these gentlemen for their cooperation and to the Cia. Minera de Penõles, S. A., for permission to publish the results of this study. The writers are also indebted to Dr. Paul F. Kerr of Columbia University for suggestions and a critical reading of the

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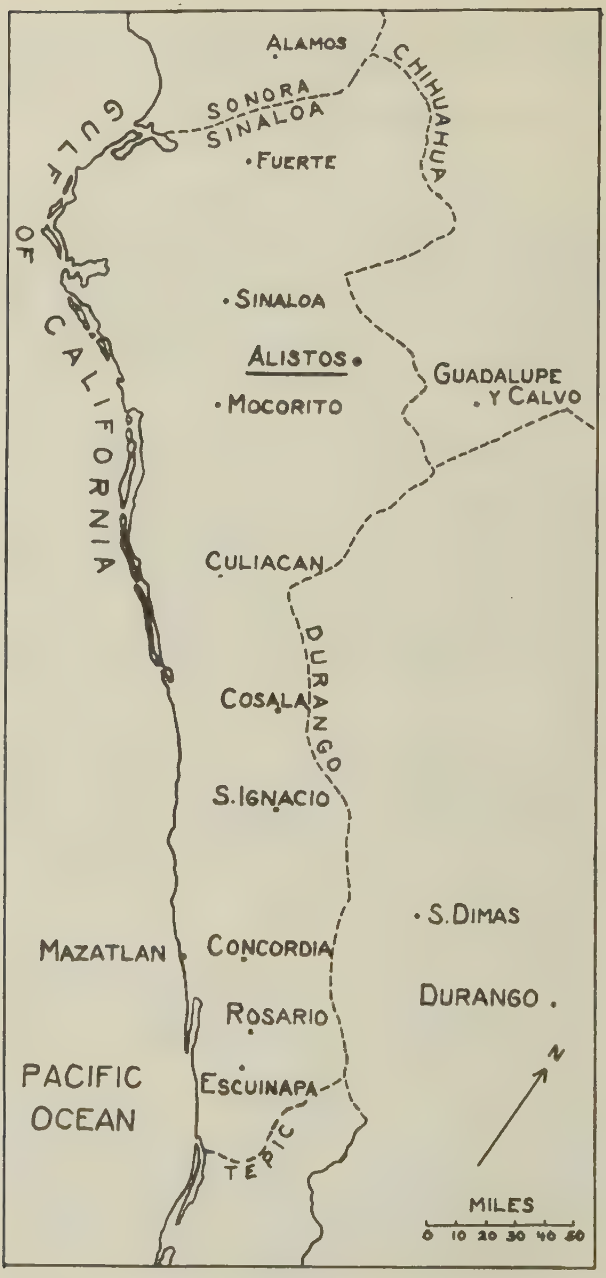

FIG. 1. Index Map.

manuscript, and for the use of *x*-ray equipment; to Dr. Charles Behre of Columbia University for reading the manuscript; and to Dr. Wilbur G. Valentine of Brooklyn College and Mr. Ralph J. Holmes of Columbia University for information and advice.

Location

The Gloria property is located at Alistos, in the Badiraguato mining district, Sinaloa, Mexico, near the boundary of Sinaloa with Chihuahua and Durango. The nearest post office is at Tameapa, 72 miles northwest of Culiacan, Sinaloa.

Field Relations

The property is situated in a region composed chiefly of deeply eroded, nearly flat-lying, Tertiary volcanic rocks consisting of andesite, latite, and rhyolite, which make up the plateau area of western Mexico (1). At Alistos they are intruded by a small peridotite stock, now largely altered to amphibole, pyroxene, serpentine, and mica.

The gold-nickel ore occurs in narrow veins within latite, near the border of the altered peridotite intrusive. Distribution of metallic constituents within the veins is highly erratic and commercial values have been found chiefly as small pockets or "bonanzas." The highest grade ore, some of which assayed up to 8.9 ounces of gold per ton and 0.90 ounces of silver, was localized near the intersection of two veins, one striking N. 35° W., the other N. 18° W. Both veins have been explored and mined for gold content some distance from the intersection, but apparently do not contain sufficient mineralization to warrant extensive development. The property is thus of interest, not so much as a commercial development of gold-nickel ore, but because of its unique and interesting mineral content.

Petrography

Examination of the rocks associated with the ore shows two fairly distinct types. One is dark green and fine grained, with a hackly fracture and smooth surfaces produced by slight slippages in the rock. In the field, rock of this type forms a small stock which has cut the surrounding volcanics. The rock has been partially metamorphosed or altered by hydrothermal solutions and thoroughly recrystallized, with introduction of pyrite and magnetite. It is believed to be an altered peridotite which is now an incipient tremolite-actinolite schist. The other rock is light buff, fine textured, and massive, and resembles a hornfels. In the field it forms a nearly horizontal sheet, believed to represent an original volcanic rock, presumably a flow, now extensively altered by hydrothermal solutions and cut by veinlets consisting chiefly of gangue minerals. It is thought to be an altered and veined enstatite latite.

Altered Peridotite. The structure of the altered peridotite is obscure and the texture variable. The rock is now composed largely of tremolite, actinolite, and other recrystallization products, such as diopside, chlorite, epidote, siderite, sericite, serpentine, and magnetite. These minerals form interlocking aggregates, many individual grains of which are as much as 2 mm. across. This texture suggests that the original rock was coarse grained. A streaking of magnetite and pyrite grains which might be regarded as an original flow structure, is believed to have formed during hydrothermal alteration and recrystallization under pressure. This belief is supported by the fact that no other original structures have been preserved.

Textures and occasional remnants indicate that the original rock was an intrusive which presumably contained pyroxene, magnetite, and perhaps some olivine, with little or no feldspar and quartz. Such a rock would fall into the general classification of peridotites, probably a pyroxenite. The rock might now be called an incipient tremolite-actinolite schist.

Enstatite Latite. Aside from the indistinct flow structure, the original structure of the latite has been largely obliterated by alteration. A number of euhedral phenocrysts of pyroxene, up to 3 mm. in diameter, were identified by their outlines. These crystals occur in a dense recrystallized matrix. In these phenocrysts there are obscure patches believed to be relicts of an original schiller structure, on which basis the mineral has been judged to be a member of the enstatite-hypersthene series. The original phenocrysts have been hydrothermally altered to aggregates of diopside, with small amounts of epidote, uralite, and carbonate.

The matrix, crystals of which average 0.05 mm. in diameter, varies from nearly pure oligoclase-andesine in places to areas in which there are are numerous diopside grains. Small amounts of orthoclase, hornblende, and apatite occur as primary minerals, but no quartz was found. Much of the feldspar may be recrystallized material. It is comparatively fresh, alteration to sericite being confined to limited areas. It is uncertain whether the diopside in the matrix is primary or an alteration product. Small quantities of zoisite and leucoxene are present as alteration materials. Kaolin occurs as a weathering product.

The enstatite latite is traversed by veinlets, the largest and oldest of which contain adularia, epidote, and pyrite. The younger veinlets are abundant and conspicuous and carry calcite associated with datolite; others contain datolite alone.

The enstatite latite is one of the nearly horizontal Tertiary volcanics of the Alistos region and has been locally intruded by the periodotite. It is not clear whether the alteration of latite and that of the peridotite are related or separate processes. Veining and introduction of adularia, epidote, pyrite, calcite, and datolite in the enstatite latite cannot be correlated with the ore mineralization, and resemble it only in the common occurrence of calcite. It is probable that the introduction was a separate process which preceded the ore mineralization. This is believed to be so because of the difference in the two types of mineralization, and because the latite was apparently crystallized and hydrothermally altered and veined before the intrusion of the peridotite. The ore occurs in veins within latite and is believed to have originated from the nearby peridotite after the alteration of the latite. The ore suite of nickel and cobalt sulphides and arsenides constituting most of the ore mineralization is one commonly associated with basic igneous rocks such as peridotites or pyroxenites. The decline in gold-nickel values away from the peridotite mass also suggests that the source of the ore was the basic igneous stock.

Mineralogy of the Ore

In the material studied, two distinct types of gold-bearing nickel ore were found. Each type is readily recognized in the hand specimen. Type 1, the gold-niccolite type, consists of massive niccolite with minor amounts of metallic associates including gold, gersdorffite and maucherite, and gangue. Type 2, the gold-millerite ore, is made up of millerite, pentlandite, gersdorffite, pyrite, and violarite, with minor amounts of gold.

The mineral association of each type of ore is distinctive. Millerite, pentlandite, and violarite do not occur in the gold-niccolite type, while niccolite and maucherite are not present in the gold-millerite type. In the material available for study gersdorffite and native gold were the only metallic minerals common to both types of ore.

Gold-Niccolite Type

Gold. In the gold-niccolite ore, gold is either associated with niccolite and gersdorffite, or is found entirely within gangue (Figs. 2, 3). It is, however, far more abundant in niccolite than in any of the other minerals. Much of the gold is quite coarse, some particles measuring up to 0.5 mm. in diameter. Etch tests indicate that the gold may contain some silver. This is supported by an assay of the ore which shows 0.90 ounce of silver, yet no silver mineral is apparent in any of the surfaces.

When associated with niccolite, gold commonly occupies an interstitial position between grain boundaries of individual crystals and replaces niccolite (Fig. 2). Gold is also found penetrating fractures in niccolite and is thus considered to be later in sequence than niccolite.

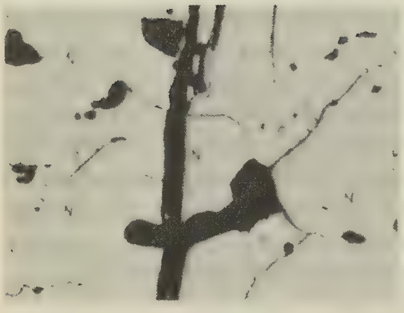

FIG. 2. Native gold (G) between grains of niccolite (N), and closely associated with gangue material (black). Maucherite rods occur in parallel orientation in the individual niccolite grains. (×78)

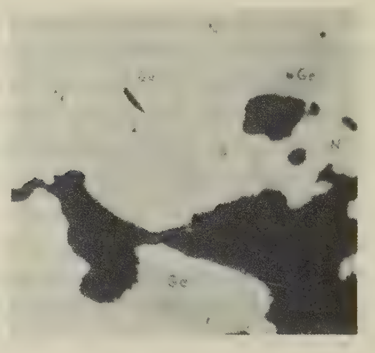

FIG. 3. Intergrowth of native gold (G) and gersdorffite (Ge) within niccolite (N). (×200)

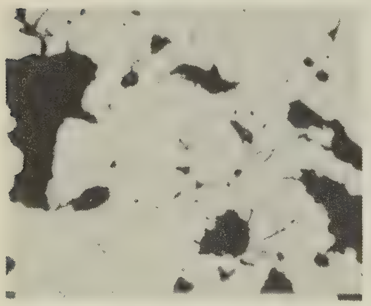

FIG. 4. Veinlets of gersdorffite (Ge) in niccolite (N) and associated with gangue (black). (×80)

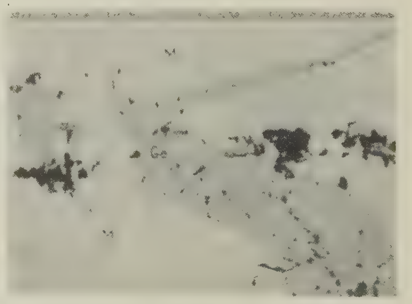

FIG. 5. Gersdorffite (Ge) veinlet in millerite (M). A small bleb of native gold (white) is seen in millerite closely associated with gersdorffite. (×138)

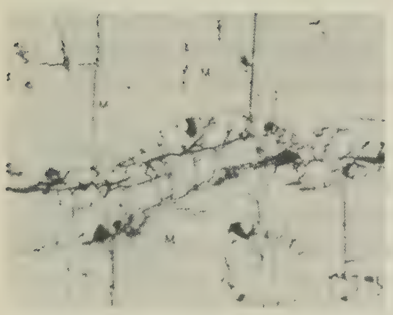

Fig. 6. Veinlet of pentlandite (P) cutting across millerite (M) grain. (×78)

Fig. 7. Stringers of pentlandite (P) oriented along twin directions in millerite (M). (×125)

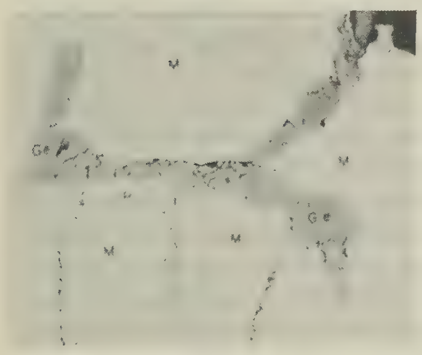

Fig. 8. Veinlets of gersdorffite (Ge) and pentlandite (P) in millerite (M). (×125)

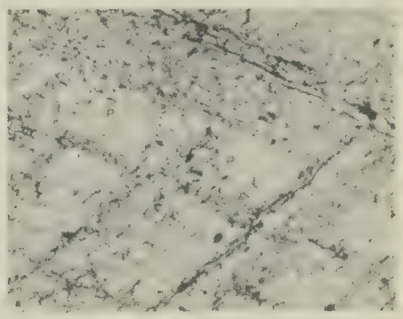

Fig. 9. Pentlandite (P) altered along cleavage directions to violarite (medium gray). (×125)

Gold is later than gersdorffite, in part at least, for it occupies small fractures in the latter. On the other hand, it is occasionally intergrown with gersdorffite in a graphic structure and the two minerals may have crystallized in part simultaneously (Fig. 3).

Niccolite. Niccolite is by far the most abundant metallic mineral and makes up approximately 90 per cent of all the metallics in this type of ore.

In the hand specimen it appears as massive, homogeneous material, often with a crude banded appearance. It is associated with dark green to black, impure carbonate, quartz, and serpentine. Gold is ordinarily not visible except with the microscope, but can sometimes be seen on examination of a polished slab with a hand lens.

Microscopic study of polished surfaces of niccolite indicate that it occurs as a mosaic of diversely oriented, interlocking grains, some of which may be 1.0 mm. or more in diameter, although the average size is about 0.5 mm. The grains exhibit the usual optical and physical properties characteristic of niccolite. Small differences in color and hardness due to orientation are distinguishable between different grains. The niccolite has been fractured and veined by gangue, commonly carbonate, and by later metallic minerals. Near the contact of the more massive niccolite with gangue, occasional skeletal outlines of niccolite are found surrounding grains of carbonate.

Maucherite. Nearly all the individual grains of niccolite contain tiny rods and blebs of a mineral identified as maucherite (Fig. 2). The small size made it impossible to obtain pure material for microchemical tests, and etch tests alone could not be considered adequate. The mineral was, however, compared with known maucherite from other localities and with niccolite and maucherite prepared synthetically by fusing known mixtures of nickel and arsenic. The synthetically formed niccolite was found to contain rods and blebs of maucherite which could be identified by microchemical and etch tests. Maucherite thus formed was similar to the material from Alistos, both as to physical properties and the manner in which it occurs within niccolite. This mode of occurrence is also consistent with known maucherite from localities described in the literature (2).

Maucherite in the Alistos ore is believed to have crystallized simultaneously with niccolite as an exsolution product. It shows no evidence of replacing niccolite, the small rods do not transgress niccolite grains, and they are oriented differently in adjacent grains (Fig. 2). These factors support an origin due to exsolution or unmixing.

Gersdorffite. Both types of ore contain a smooth, hard, white, isotropic mineral with well developed cubical cleavage. Microchemical tests show the presence of nickel and arsenic, and *x*-ray diffraction patterns correspond to those of gersdorffite from Müsen, Germany, and Liebenstein, Saxony. The mineral is present as irregular patches and veins within niccolite, and distinctly penetrates and replaces niccolite along fractures, between grain boundaries, and along the contact between niccolite and gangue (Fig. 4). Gold is sometimes associated with gersdorffite as mentioned above.

Although present in all the polished surfaces studied, gersdorffite makes up but a small proportion of the total metallic mineral content.

As both niccolite and maucherite are arsenides of nickel, and gersdorffite is the only sulphide observed in this type of ore, it would indicate that sulphur is present in but minor quantity.

Gangue. The first generation of gangue was deposited prior to any of the ore minerals. It consists largely of a fine mosaic of calcite, siderite, and chlorite. This was followed by the introduction of niccolite and maucherite. After the niccolite had crystallized, fracturing and shattering took place affecting both the gangue and niccolite. Along these fractures calcite, ilvaite, gersdorffite, and gold were deposited (Figs. 2, 4). Deposition of these minerals was followed by another period of fracturing, and the cracks were then filled with calcite and actinolite.

Oxidation Products. Oxidation has been slight and developed principally as a green coating of annabergite on some of the niccolite. It has affected the ore to a thickness of less than 1 mm. The minerals formed in addition to annabergite are jarosite and limonite. There are also some semi-opaque sugary-white patches forming an indefinite alteration aggregate, an indeterminable reddish aggregate, and a black sooty substance. A small amount of chlorite is present in the gangue and in the oxidized products. In places the chlorite occurs in small, ovoid, limonite-stained areas most of which are isotropic, but some show a spherulitic structure and give a poor interference figure. This may be either a late primary mineral or an oxidation product.

Gold-Millerite Type

The gold-millerite ore is believed to be hypogene in origin. This is supported by the following data: The occurrence of gersdorffite and gold in both types of ore; the massive, twinned character of millerite; and the fact that pentlandite cuts the millerite. Gersdorffite is said to be occasionally secondary but this, however, is rare (3). Its association with niccolite and maucherite is hypogene and it is probably also hypogene in the millerite ore. Millerite is usually supergene (4) but the possibility of hypogene origin has been recognized (2), and pentlandite may be supergene at times although no entirely satisfactory evidence has been presented for this belief (5). The massive crystalline, non-fibrous character and early crystallization of millerite, however, and the fact that both millerite and pentlandite are cut by gersdorffite, indicate a probable hypogene origin.

Gold. Only two or three specks of native gold were found in surfaces of this type of ore. These occurred within grains of millerite and do not, therefore, add much to the paragenetic relations (Fig. 5). Because of the association of gold with gersdorffite veinlets, although not actually part of the veinlets, it is thought that the two minerals are closely related in time of deposition. This is supported by the simultaneous crystallization, in part, of gold and gersdorffite in the gold-niccolite ore.

Millerite. Millerite is the most abundant constituent in this type of ore. It lacks the usual fibrous structure characteristic of most millerite and is coarsely crystalline, somewhat massive, and exhibits excellent cleavage and polysynthetic twinning. Identification was confirmed by microchemical and etch tests, optical properties, and x-ray diffraction patterns compared with patterns of known millerite. It is judged to be hypogene because of its character and the fact that it is cut by veinlets of both pentlandite and gersdorffite.

Since millerite does not occur in the gold-niccolite ore its paragenetic relations with respect to niccolite could not be determined. It precedes both pentlandite and gersdorffite, however, and is thus judged to be one of the earlier metallic minerals.

Pentlandite. Pentlandite is abundant in the gold-millerite ore. It occurs as broad, irregular veinlets and patches in millerite, some of which may be several millimeters in length (Fig. 6), and as short, narrow, vein-like stringers almost invariably oriented along cleavage or twinning directions in the millerite (Fig. 7). Octahedral cleavage and irregular fractures are prominent in both varieties of the mineral.

The larger veinlets and masses of pentlandite are clearly later than millerite for they penetrate and replace the latter conspicuously. With regard to the smaller stringers, however, the evidence for replacement is far from conclusive. The stringers are so persistently oriented along cleavage and twin directions that it is believed they may represent an exsolution product; the millerite and pentlandite having crystallized simultaneously. The larger veinlets and masses of pentlandite are thought to represent deposition from a slightly later iron- and nickel-bearing solution.

Violarite. Pentlandite, particularly the larger masses, shows extensive alteration to violarite. Matted intergrowths of the latter penetrate along cleavages and fractures in pentlandite, often leaving a residual core of unreplaced pentlandite in a mass of violarite (Fig. 9). In all cases this alteration stops abruptly at the contact of millerite or gersdorffite. Violarite probably formed by supergene alteration of pentlandite (2, 6).

Because of the occurrence of violarite in minute areas, pure material could not be obtained for chemical or x-ray study. It was impossible, therefore, to distinguish with certainty between violarite and bravoite. The appearance, properties, and absence of intergrown pyrite or marcasite, however, are more typical of violarite than of bravoite (2, 5, 6, 7, 9, 11).

Gersdorffite. Gersdorffite has the same occurrence and appearance in the gold-millerite ore as in the gold-niccolite type. It crystallized later than millerite and may be closely related in time of deposition with the gold (Figs. 5, 8). No evidence of the paragenetic relation of gersdorffite to gold was found, but it is somewhat later than pentlandite because veinlets of gersdorffite cut across areas of pentlandite.

Pyrite. A considerable amount of pyrite is present in parts of the gold-millerite ore. It occurs in irregular, branching veinlets replacing pentlandite. Upon reaching an area of millerite or gersdorffite, the pyrite stops abruptly. Pyrite has thus selectively replaced pentlandite and has crystallized after the other minerals, with the exception of violarite. It tarnishes rapidly, and, judging from some of the thin sections of oxidized ore, is altering to limonite. This alteration was not observed in polished surfaces of unoxidized ore.

Gangue. The gold-millerite ore occurs along fractures and as replacing veinlets in the early gangue material which consists of fine granular calcite. After deposition of millerite, the pentlandite, gold, and gersdorffite were introduced along with some calcite. This was followed by deposition of coarse calcite along fractures in the millerite and early gangue material.

Oxidation Products. The oxidized material consists primarily of erythrite, jarosite, and limonite. Apparently erythrite formed by oxidation of millerite because it occurs along fractures and surrounding the borders of some millerite grains. This would indicate that millerite contained cobalt, probably partly replacing nickel. Jarosite is closely associated with pyrite and may represent alteration by potash-bearing waters derived from rocks associated with the ore.

PARAGENESIS

Gold-Niccolite Ore. Mineralization of the enstatite latite began with the introduction of a mosaic of calcite, siderite, and chlorite. It is difficult to determine how much, if any, of the early gangue material represents highly altered and replaced original rock. Certain patches and streaks, however, contain a large amount of chlorite, in some of which there is a suggestion of an antecedent interlocking crystalline rock structure. The early gangue was followed by the introduction of veins of niccolite and maucherite. Next, fracturing and shattering took place and along the fractures coarse clear calcite, ilvaite, gold, and gersdorffite were deposited. Gold is in part contemporaneous with gersdorffite, because it occurs in graphic intergrowth with the latter. Gold is also in part later than gersdorffite for it occasionally occupies fractures in it. After the deposition of these minerals, fracturing again occurred and the cracks were filled with calcite and a green, fibrous mineral. This mineral tends to form rosettes and may be actinolite or an iron or nickel-iron arsenate.

Gold-Millerite Ore. In this type of ore millerite was the first metallic mineral to crystallize. It occurs along fractures and as a replacing mineral in the early gangue which consists of calcite. Millerite was followed by the introduction of pentlandite, gersdorffite, gold, pyrite, and probably some calcite. Pyrite was the last metallic mineral to form, with the exception of violarite which is a supergene alteration product of pentlandite. Pyrite occurs rimming and replacing pentlandite, but has not affected any of the other minerals. This replacement is apparently selective because gersdorffite and millerite have not been replaced or intruded. The few specks of gold in this ore occur within millerite and closely associated with, but not actually in, veinlets of gersdorffite. The association and the fact that gold is intergrown with gersdorffite in the niccolite ore, suggest that it is also associated in time of deposition in this ore. The introduction of pentlandite, gersdorffite, gold, and pyrite apparently was accompanied by the deposition of a small amount of fine granular calcite. Following the deposition of these minerals fracturing occurred and the cracks were filled with coarse calcite.

Origin of the Ore

It is believed that the source of the gold-nickel ore was the small peridotite or pyroxenite stock cutting the Tertiary volcanic rocks in the vicinity of Alistos. The ore occurs near the border of the peridotite mass in veins within enstatite latite. The occurrence of considerable amounts of nickel sulphides and arsenides, and of a trace of platinum in the assayed gold-niccolite ore, suggest an association with a basic igneous intrusive—in this case peridotite. Exploratory work also indicates that the greatest ore concentration is at the intersection of two veins near the peridotite mass. Ore mineralization decreases away from the peridotite to such an extent that further development of the deposit was discouraged.

It seems probable that the ore minerals were introduced by hydrothermal solutions (7). End-stage solutions of the magma attacked the peridotite and altered and recrystallized it under pressure to a rock composed of amphibole, pyroxene, serpentine, magnetite, and mica. The source of the water required for the formation of amphibole and mica, and the carbon dioxide of the calcite may have been circulating ground waters. This is suggested because peridotite magmas are thought to be low in water content (8), and no acid igneous rock younger than the peridotite occurs in the immediate area of the Alistos deposit.

The peridotite apparently contained a small amount of nickel which may have been present largely in the olivine. Nickel, calcium, and possibly all of the gold were later taken into solution by hydrothermal attack on the peridotite, and deposited in the latite as veins of nickel sulphides and arsenides and free gold. Some or all of the gold may have been introduced from another source, but the close intergrowths with gersdorffite do not support this assumption, nor is there any other evidence for such a belief. It is thus thought that hydrothermal alteration of the peridotite produced solution of minerals of the rock which were then redeposited in veins in the latite.

Comparison with Other Deposits

Although the mineralogy of the Alistos deposit is believed to be unique, the hydrothermal origin and association with a basic intrusive have been described in other occurrences. At the nickel-gold deposit near Mount Vernon, Skagit County, Washington, a serpentinized peridotite is intrusive into metamorphosed pre-Tertiary sediments (7). A tabular body of silica-carbonate rock is locally brecciated and contains a cement of sulphides, carbonates, and quartz. In the description of the deposit, Hobbs and Pecora state that they believe "the nickel was originally present in the serpentinized peridotite and that it was dissolved and redistributed by ascending hydrothermal gold-bearing solutions while the serpentine mass was being altered into the silica-carbonate rock."

The Mount Vernon deposit is similar to the Alistos occurrence in that native gold is associated with carbonates, pyrite, and serpentine minerals. The rest of the mineralogy, however, is essentially different and consists of quartz, opal, chalcedony, marcasite, bravoite, and chromite. Marcasite contains a trace of nickel and is the most abundant sulphide. The presence of a silica-carbonate rock composed of the above mentioned silica minerals and carbonates, with minor amounts of iron oxides and chromite differs from anything at Alistos. The authors believe that the silica-carbonate rock "was formed by intense alteration of a serpentinized peridotite along a shear zone" (7).

Although it contains no native gold, the Copper King mine near Gold Hill, Boulder County, Colorado, more nearly resembles the Alistos deposit in mineralogy than does any other occurrence (9). The ore consists of the nickel minerals polydymite, pentlandite, millerite, niccolite, bravoite, and violarite associated with cobaltite, pyrite, pyrrhotite, chalcopyrite, sphalerite, arsenopyrite, and quartz. The ore occurs "in a lenticular layer of amphibolite in biotite schist of the Idaho Springs formation, half a mile west of the border of a small batholith of the pre-Cambrian Boulder Creek granite. A dike-like body of hornblende-quartz gabbro, related to the granite, is exposed in the lower workings, and many irregular pegmatite dikes cut the schist, amphibolite, and gabbro." The authors believe that "the nickel ore is genetically related to the gabbro" (9).

Although the mineralogy of the Copper King deposit is somewhat similar to that at Alistos, the association and concentration differ markedly. Polydymite is the chief primary nickel mineral at Copper King, whereas niccolite and millerite are most abundant at Alistos. Millerite is apparently supergene at Copper King; it is believed to be hypogene at Alistos. Also, pyrrhotite, cobaltite, chalcopyrite, and sphalerite are absent from the Alistos material and considerable gold is present.

There are several other deposits which resemble the Alistos occurrence in certain particulars (6, 10, 13). The association and occurrence of native gold in niccolite and in hypogene millerite, the presence of hypogene millerite, and the graphic intergrowth of gold and gersdorffite are believed to differ from any other described occurrences.

Summary and Conclusions

The Alistos gold-nickel deposit is unusual in its mineral assemblage. Native gold is associated with two types of ore both of which are considered to be hypogene: A niccolite type containing maucherite and gersdorffite, and a millerite type containing pentlandite, gersdorffite, pyrite, and supergene violarite. No pyrrhotite was found in either type of ore (14).

Two rocks are intimately associated in the field with the ore mineralization; an enstatite latite and a peridotite or pyroxenite. The latite has been altered by hydrothermal attack to a rock composed principally of enstatite, diopside, uralite, epidote, orthoclase, and carbonate. End-stage solutions altered the peridotite to an aggregate of tremolite, actinolite, pyroxene, chlorite, epidote, serpentine, and magnetite. Latite is one of the Tertiary flat-lying volcanics of the Alistos district and has been intruded by the peridotite. Introduction of ore minerals probably took place as the last phase of the hydrothermal alteration of the peridotite.

There is little oxidation of either type of ore. The gold-niccolite ore contains a small amount of annabergite, jarosite, limonite, one or two unidentified aggregates, and some chlorite which may be primary or an alteration product. The gold-millerite ore contains a minor quantity of erythrite, jarosite, and limonite.

Paragenesis of the gold-niccolite ore is as follows: Deposition of carbonate and chlorite gangue was followed in order by niccolite and maucherite; then fracturing and shattering; introduction of calcite, ilvaite, gold and gersdorffite; again fracturing; deposition of calcite and possibly actinolite. In the gold-millerite ore, fine granular calcite was followed by millerite; then in order by pentlandite, gersdorffite and gold, and pyrite. These were followed by a period of fracturing and the introduction of coarse calcite. Violarite was the last mineral to form and is believed to be supergene.

The ore minerals are thought to have originated from the peridotite stock by hydrothermal alteration. End-stage solutions from the peridotite magma, perhaps mixed with circulating ground waters, removed nickel and probably gold from the peridotite and deposited them in the latite as veins of nickel arsenides and sulphides, and native gold.

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SETTLING OF HEAVY MINERALS IN A GRANODIORITE DIKE AT BRADFORD, RHODE ISLAND

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ABSTRACT

A granodiorite dike at Bradford, Rhode Island, has a thickness of sixty-five feet, an east-west strike, and a dip of 28° south. The rock appears to be uniform, except for zones at the upper and lower contacts.

A two-foot zone at the upper contact is pegmatitic in texture, poor in heavy minerals, and rich in muscovite. It is explained as being due to hydrothermal action.

Heavy mineral separations of samples from different parts of the dike indicate that the proportion of heavy minerals increases systematically toward the base of the dike. This is also shown by thin-section studies of specimens from different parts of the dike, and by studies of a dark zone at the base of the dike. The systematic increase of heavy minerals toward the base seems to be due to crystal settling, for the following reasons. (1) The minerals which are concentrated toward the base are heavier than the magma of granodiorite. (2) These minerals crystallized early in the solidification of the rock. (3) In the dark zone at the base, the greatest concentrations of heavy minerals are in the small depressions, as might be expected from the settling of crystals on a slightly irregular floor. (4) An alternative origin by hydrothermal solutions is opposed by the fact that the variations extend through the body of the rock and that the main concentration is in the lower part of the dike.

The small size of the settled grains, with zircon as small as .10 by .03 mm. indicates a low viscosity of the magma.

INTRODUCTION

Studies of heavy minerals in a granodiorite dike at Bradford, Rhode Island (Niantic on the Charlestown sheet of the United States Geological Survey topographic map), were begun in part for the purpose of teaching students the technique of heavy mineral separation, and in part to see if there were any variations in the heavy minerals of what appears to be a very uniform rock mass.

The chief advantages of this dike for study are: (1) the apparent uniformity of the rock throughout the dike indicates that it is one simple intrusion; (2) quarrying operations at the Sullivan Quarry have exposed a great deal of fresh rock at various positions in the dike; and (3) the limited size makes possible a fairly complete study.

RELATIONSHIPS

This is one of several fine-grained dikes in the Westerly area (Dale, 1923 and Martin, 1925). The dike which is about a half-mile south of Bradford is approximately sixty-five feet thick, dips south about twenty-eight degrees, and strikes about east-west. It cuts sharply across the foliation of the Sterling granite gneiss, which stands almost vertical and strikes about east-west.

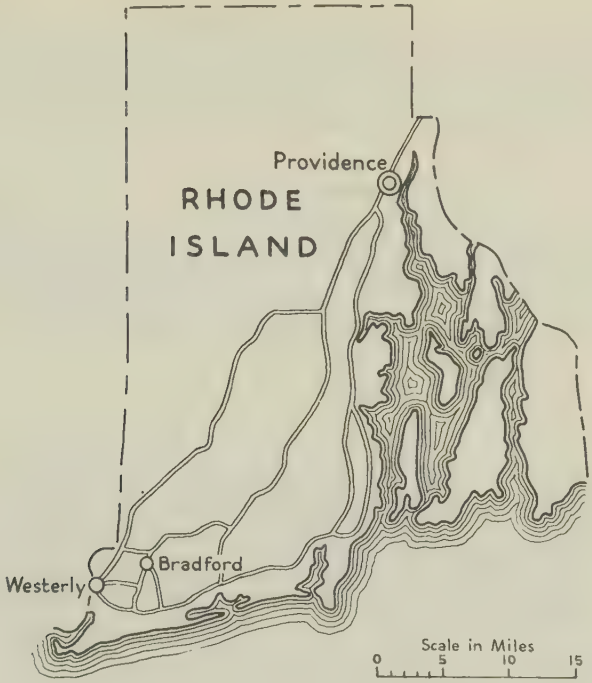

FIG. 1. Map showing location of Bradford.

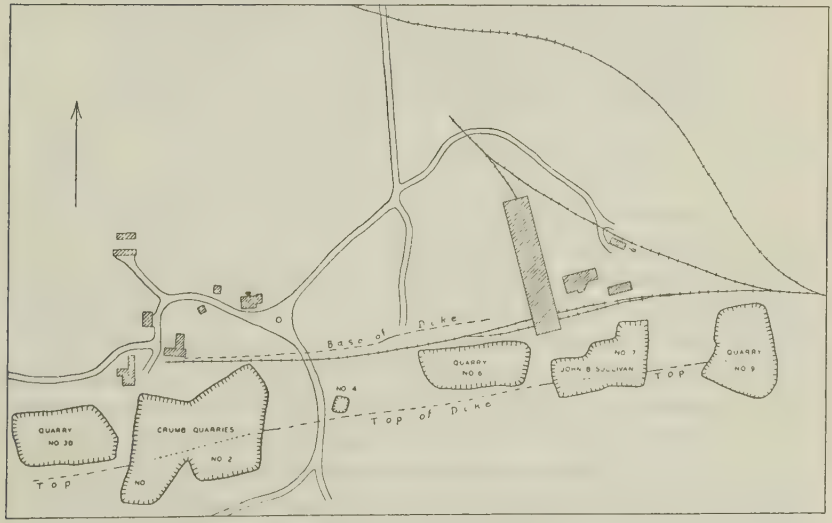

FIG. 2. Quarries in granodiorite dike at Bradford.

This dike is probably of post-Carboniferous age as it is petrographically similar to the granitic intrusions which cut the Carboniferous sedimentary rocks along the west shores of Narragansett Bay fifteen to twenty miles to the east and northeast of Bradford (Loughlin, 1910).

METHODS OF STUDY

The methods used for study of the variations within the dike were: (1) field observations, (2) thin-section studies for Rosiwal analysis and for determining the order of crystallization, and (3) heavy mineral studies. Only the methods of heavy mineral study need description.

Methods of heavy mineral separation.

In the heavy mineral separations a greater effort was made to obtain uniformity than extreme accuracy.

At first, samples of approximately 100 grams were crushed to pass a 40-mesh screen with openings of about 0.5 mm. (Taylor, 1937). The samples were washed to remove the fine dust. The heavy minerals were then separated with bromoform (specific gravity 2.82) in a centrifuge. There were almost no light minerals in the heavy portion, but a few biotite flakes remained in the light portion. At first, only 25 grams of the 100-gram sample were separated by individual students, but eventually the whole sample was used and the percentages given in Table 1 are from these totals. In some of the later samples only 25 to 40 grams were taken and the whole sample separated. The author performed part or all of the work on each sample.

Certain of the heavy mineral fractions were separated according to magnetic properties. The strongly magnetic portion was removed by a small "alnico" magnet. Further separation was accomplished by use of a Franz Isodynamic Separator. The heavy minerals were thus divided into strongly magnetic, moderately magnetic, and non-magnetic portions and the weight of each was determined.

The non-magnetic fraction was further studied to determine roughly the percentages of muscovite, apatite, sphene, and zircon. Small amounts of the fractions were immersed in an appropriate oil, random traverses of the field were made, and the length of the intercepts of the grains were taken as a volumetric measure of the percentages of the different minerals. The volumes were calculated to weight percentages. This method, obviously, does not give an accurate measure of the amounts of the different minerals present, but it probably gives comparable results. It should be noted that the percentages of the individual minerals in Table 1 are only estimated.

Field Observations

The rock of the dike is bluish-gray or gray in color. The texture is even grained with the crystals measuring one to three millimeters across. The constituents visible to the unaided eye are: feldspars, quartz, and biotite. The rock is widely known for its attractive appearance, both on polished and on hammered surfaces. With the exception of the lower and upper contact zones, the rock of the dike is remarkably uniform. Specimens from different parts of the dike match very well and only rarely does one see dark or light streaks in the blocks about the yard or in the quarry. No evidence of a chilled border is present.

The dike as exposed in the Sullivan Quarry is more uniform than are most of the dikes in the vicinity of Westerly. The upper contact, where exposed in the main working pit, is almost a plane surface. The lower contact, which is not well exposed in the Sullivan pit, but which is exposed at several places in the Crumb Quarry to the west, undulates with departures of two or three feet from a plane. This lower contact is very sharp and is marked by a dark zone of heavy minerals (See Fig. 3). The main dark zone is only an eighth to a quarter of an inch thick, but a transition zone, two to three inches thick, is streaky and somewhat darker than the ordinary granodiorite above. The Sterling granite gneiss, just below the contact, has a half-inch bleached zone which is poor in biotite, somewhat enriched in magnetite, and somewhat coarser in texture. At the upper contact of the dike is a zone two to four feet thick in which the granodiorite is pink, poor in dark minerals, somewhat richer in muscovite, coarser in texture, and somewhat pegmatitic.

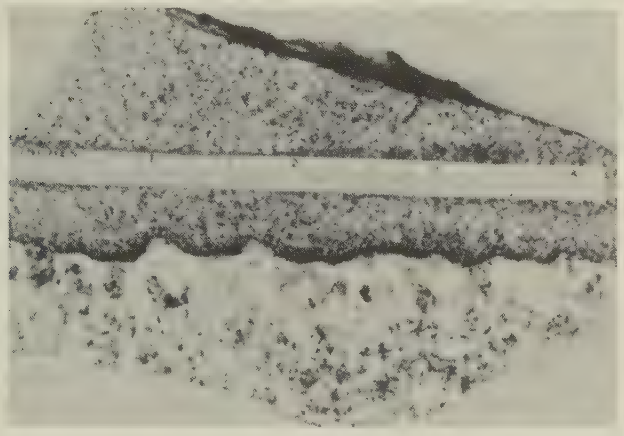

Fig. 3. Photograph of dark zone at base of dike.

Small pegmatites and aplite dikes are common here, especially in the enclosing Sterling granite gneiss.

PETROGRAPHY

Main constituents.

The texture is irregular, with considerable variation in grain-size. The main constituent is oligoclase (An_{18-22}), which shows some zoning. The small variations in the composition of the plagioclase do not seem to be systematic with respect to the position within the dike. There is some tendency for the oligoclase to show crystal outlines. Carlsbad twins are common. The potash feldspar is microcline, some of which is perthitic. A few grains of it surround the oligoclase. Quartz is in part interstitial and seems to embay the feldspars as though partially replacing them. Biotite has a considerable tendency to be bounded by the base. Some grains appear to have crystallized early and some appear to have formed as later replacements of oligoclase. The β and γ indices range between 1.630 and 1.635, 2V is small, the optic sign is negative, and the pleochroism is in dark greenish brown and pale golden. No systematic variations in the optical properties were discovered. Some is altered to chlorite. Muscovite is uncommon, except in the upper contact zone. The order of crystallization appears to be: biotite, oligoclase, microcline, and quartz. The rock is a granodiorite, as is indicated by the modes of Table 2.

Accessory minerals.

The chief accessory minerals are listed below. In addition to these more abundant ones, there are a very few grains of pyrite and rutile.

Allanite

Allanite is present in a very few scattered crystals. It is yellowish-brown, pleochroic, and usually shows pronounced zoning. The indices of refraction vary between different crystals and within one crystal. Observed indices of refraction ranged from 1.63 to 1.68. The birefringence is about .010 to .015. The optic sign is negative and 2V is large. Crystals are commonly enclosed by early biotite, which has pleochroic haloes around the allanite. This relationship to the biotite and the euhedral form indicate that the allanite formed early. The lengths of measured crystals varied from .10 to .40 mm. and the widths from .03 to .22 mm.

Apatite

Apatite is present as tiny needles and as larger round grains. Certain of the grains are included in early biotite. Crystals in thin section measured $.19 \times .09$; $.15 \times .10$; $08 \times .02$ mm.

Magnetite

Much of the magnetite is in irregular grains, but some grains show crystal boundaries. Textural relations are indeterminate, but they suggest that some of the magnetite formed early and some late. Some of this material shows leucoxenic alteration, so it is probably ilmenite. The largest grains measured .30 mm. in diameter.

Sphene

Sphene is present in irregular grains, and diamond-shaped or wedge-shaped crystals. Some crystals are enclosed by early biotite. The intermediate index of refraction, 1.896 ±.002, indicates that it is sphene. A similar mineral in the enclosing Sterling granite gneiss has an intermediate index of 1.878±.002, which is nearer to that of keilhauite (Young 1938). The sphene of the granodiorite has many tiny inclusions, whereas the keilhauite is almost free of inclusions. The largest grains measured .24 mm. in diameter.

Zircon

Zircon is generally in good crystals, many of which are within pleochroic haloes in early biotite. Representative grains measured .21×.03; .13×.03 and .06×.02 mm.

Order of crystallization of accessory minerals.

The textural relationships indicate that allanite, apatite, zircon, most of the biotite, and some of the sphene crystallized early. Some of the magnetite may also have formed early.

RESULTS

The distribution of minerals in this dike is indicated by: (1) heavy mineral separations (total heavy mineral fractions and individual minerals), (2) thin-section studies, and (3) by a special thin-section study of material from the lower dark zone (21 in Table 2) obtained from the well-exposed base in the abandoned Crumb Quarry to the west of the main working pit.

Totals of heavy mineral fractions.

The most obvious feature, which first attacted attention in the course of the work, is that the lowest samples, and especially those nearest the base of the dike, have the largest percentages of heavy minerals. The series 1, 2, 3, and 4, show this especially well. There are a number of exceptions, as at 5 and 15. No satisfactory explanation for these has occurred to the writer, but a very few vague dark and light streaks have been seen in blocks about the yard. These erratic samples may have come from such a zone which was not noticed when the sampling was done. An apparent exception is 10, which appears to have too small a heavy mineral fraction. The sample was taken from a large block on a shelf at the west side of the quarry. At the time the sample was taken it was thought that the block had come from an adjacent wall. A re-examination showed, however, that it certainly did not come from that position and the conclusion is reached that it came from some location higher on the quarry wall. All other samples were taken from the walls of the quarry and not from loose blocks. Thus, the total heavy fractions show, with few exceptions, a systematic increase toward the lower contact of the dike.

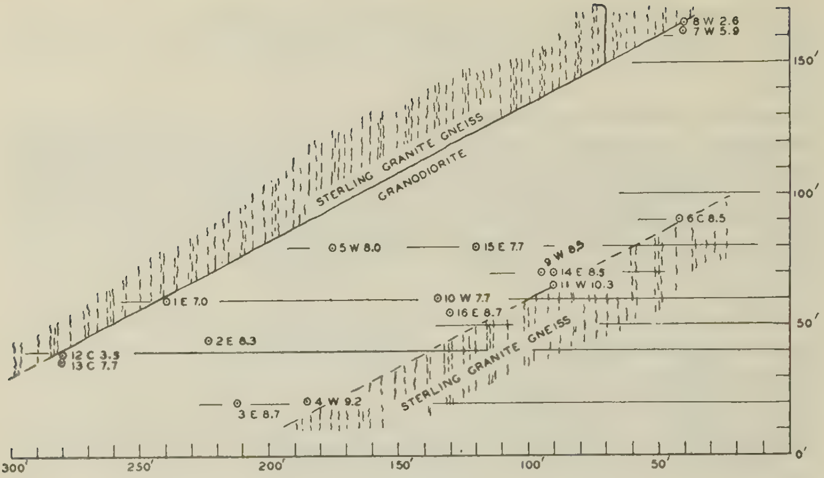

FIG. 4. Cross section of Bradford dike at Sullivan quarry. Numbers show positions of samples (1 to 16); whether from east wall (E), west wall (W), or center (C) of quarry; and per cent of heavy minerals. Distances and elevations in feet, but not referred to a known datum.

TABLE 1. HEAVY MINERALS

Sample No.	Weight of sample	Percentage by weight—heavier than bromoform (2.82)			Non-magnetic (amounts of individual minerals estimated)					
		Total	Strongly magnetic (magnetite)	Moderately magnetic (biotite & allanite)	Total	Muscovite	Zircon	Sphene	Apatite	Total excluding muscovite
1	30.87 g.	7.0	1.2	5.4	.39	.31	.01	.04	.03	.08
2	83.20 g.	8.3	1.3	6.3	.73	.47	.04	.19	.03	.26
3	69.44 g.	8.7	1.2	6.9	.67	.29	.05	.21	.12	.38
4	80.00 g.	9.2	1.2	7.3	.70	.49	.06	.04	.11	.21
5	125.48 g.	8.0								
6	81.12 g.	8.5								
7	25.00 g.	5.9								
8	25.00 g.	2.6								
9	100.00 g.	8.5								
10	100.00 g.	7.7								
11	32.75 g.	10.3	1.7	7.7	.93	.13	.09	.54	.17	.80
12	24.08 g.	3.5								
13	26.52 g.	7.7								
14	23.00 g.	8.5								
15	64.55 g.	7.7								
16	36.66 g.	8.7								

TABLE 2. MODES FROM THIN SECTIONS—PERCENTAGE BY VOLUME

Specimen No.	Microcline	Oligoclase	Quartz	Biotite	Muscovite	Magnetite	Accessories excluding allanite	Allanite
1	23	39	31	6		1		
2	25	41	27	5	1		1	
3	28	44	19	8			1	
4	27	45	19	8			1	
12	37	37	25	1				
13	27	42	25	5			1	
21	22	33	10	15		15	1	4

Individual minerals.

Allanite is not readily found in the heavy fractions and is too scattered to show systematically in thin sections, but is greatly concentrated in the dark zone at the base, as shown by thin section 21.

Apatite shows some concentration in the bottom dark zone and some in the lower heavy fractions, as shown in Table 1.

Biotite shows an increase toward the base by all of these observations.

Because of its high specific gravity, magnetite might be expected to be concentrated most by settling, but it shows only slight variations in the heavy fractions of Table 1. It shows a strong concentration in the bottom dark zone, however (see 21 of Table 2). These results indicate that some of the magnetite is concentrated toward the base and some is not, which agrees with the textural evidence that some formed early and some late. The presence of a number of magnetite grains in the Sterling granite gneiss just below the lower contact of the dike indicates that some of it may have a hydrothermal origin.

Muscovite, from observations in the quarry, appears to be concentrated along the bleached zone at the upper contact. It probably has a hydrothermal origin. Its distribution is irregular in thin sections and in the heavy fractions. There is very little of it in the lower dark zone.

Sphene is somewhat concentrated in the lower heavy fractions of Table 1, but shows some unsystematic variation. It is definitely more abundant in the bottom dark zone.

Zircon shows a regular and systematic abundance in the lower heavy fractions of Table 1 and is concentrated in the bottom dark zone.

A study of the modes of Table 2 shows that there is also a systematic variation of the main constituents. The most definite variations are the increase of plagioclase and the decrease of quartz toward the base. The determination of quartz is probably the most reliable and it is the most systematic.

Explanation

The pegmatitic texture, the bleaching, and the concentration of muscovite in the zone at the upper contact appear to have been caused by pegmatitic or hydrothermal solutions which traveled upward along the contact. Some of the magnetite in the Sterling granite gneiss at the lower contact, and in the lower dark zone, may also have been caused by hydrothermal solutions.

The other variations appear to have been caused by crystal settling, for the reasons given below.

(1) The minerals which are concentrated toward the base are heavy minerals. The mean specific gravities as given in the *Handbook of Physical Constants* (Birch and others 1942) are: allanite 3.5, apatite 3.2, biotite 2.9, magnetite 5.1, sphene 3.5 (from Dana's *Textbook of Mineralogy*, as it is not listed in the *Handbook*), and zircon 4.4. The specific gravity of the granodiorite ranges from 2.64 to 2.67, and the magma must have had a lower specific gravity. It is apparent from this that the settled minerals had considerably greater specific gravities than the granodiorite magma.

(2) The minerals which are concentrated toward the base are minerals which generally form early in igneous rocks. Allanite, apatite, zircon, most of the biotite and some of the sphene have textural relations which indicate that they were formed early in this rock.

(3) In the dark zone at the base, the greatest concentrations of heavy minerals are in the small depressions, as is to be expected from the settling of crystals on a slightly irregular floor. This is shown even in a hand specimen (see Fig. 3). The crystals lie in this lower zone as though they had settled there.

(4) The following evidence opposes the alternative origin by hydrothermal solutions. The variations extend throughout the body of the rock where there is no accompanying evidence of hydrothermal action. The main concentration is at the base, whereas hydrothermal action would ordinarily be at the top. The upper bleached and pegmatitic zone shows that the main hydrothermal action was at the top in this dike.

The size of the crystals of heavy minerals might be expected to increase toward the base, but no such increase was observed either in thin section or in the heavy fractions. This may be due to the fact that most of these minerals are too scarce for adequate observation in thin section and that the larger grains are more likely to be broken during crushing.

A further conclusion from these results is that the viscosity of this magma was very low. The sinking of zircon crystals as small as .10 by .03 mm. is only possible in a liquid of considerable fluidity.

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NEW MINERAL NAMES

Inderborite

G. S. Gorshkov: A new mineral from the region of Lake Inder. *Compt. Rend. Acad. Sci. U.R.S.S.*, **33,** 254–256 (1941).

N. J. Ikornikova and M. N. Godlevsky: The new borate—metahydroboracite. *Compt. Rend. Acad. Sci. U.R.S.S.*, **33,** 257–258 (1941).

Name: For the locality and the composition. An editorial note states that Gorshkov's article was submitted May 27, 1941, and that of Ikornikova and Godlevsky on July 26, 1941. Hence the name inderborite has priority and the name metahydroboracite should be dropped.

Chemical Properties: Composition $CaMgB_6O_{11}\cdot 11H_2O$. Analysis: CaO 11.27, MgO 8.00, B_2O_3 41.70, ignition loss 39.48; Sum 100.45% (G); CaO 11.16, MgO 8.01, B_2O_3 40.90, ignition loss 39.54, F none, Insol. 0.01, R_2O_3 0.02; Sum 99.64% (M. M. Tikhomirova quoted by 1. and G.). Before the blowpipe, cracks and fuses to a colorless glass, giving a light green flame. "Very poorly soluble in water and cold acid," dissolves quickly in hot HCl.

Crystallographic Properties: Monoclinic, prismatic.

$$a:b:c=1.6346:1:1.3173,\ \beta=90°48' \text{ (G.)}$$
$$a:b:c=1.6395:1:2.6346,\ \beta=90°44\tfrac{1}{2}' \text{ (I. and G.)}$$

The forms $\{100\}$, $\{001\}$, $\{110\}$, $\{221\}$, $\{\bar{2}21\}$, $\{111\}$, $\{\bar{1}11\}$ and $\{\bar{1}12\}$ were noted (G.). Found as coarsely crystalline aggregates and well developed crystals up to 2 cm. in size.

Physical Properties: Colorless to white, transparent to semitransparent. Luster vitreous. Cleavage $\{100\}$ clearly manifest (G.), $\{100\}$ perfect (I. and G.). Fracture conchoidal (G.). Hardness $=2\frac{1}{2}$ (G.), $3\frac{1}{2}$ (I. and G.). Specific gravity $=1.928$–1.930 (G.), 2.004 (I. and G.).

Optical Properties: Optically negative.

$$\alpha=1.496,\ \beta=1.521,\ \gamma=1.538\text{–}1.544,\ 2V=80\text{–}86° \text{ (G.)}$$
$$\alpha=1.483,\ \beta=1.512,\ \gamma=1.530 \text{ (all } \pm.002\text{, Na light)},\ 2V=77° \text{ (I. and G.)}$$

The determinations by G.: α and β by immersion, γ calculated from 2V. $\gamma=b$, $\alpha\wedge c=0$–$1°$ (G.), $2\frac{1}{2}°$ (I. and G.).

Occurrence: Occurs at the borate deposits of Inder Lake, Gurviev region, Kazakh S.S.R. Associated minerals are inyoite, colemanite and ulexite which are secondary in relation to inderborite (G.), inyoite and szaibelyite (I. and G.).

Relationships: A member of the hexaborate group which includes

Veatchite	$Ca_2B_6O_{11}\cdot 6H_2O$	Hydroboracite	$CaMgB_6O_{11}\cdot 6H_2O$
Colemanite	$Ca_2B_6O_{11}\cdot 5H_2O$	Inderborite	$CaMgB_6O_{11}\cdot 11H_2O$
Meyerhofferite	$Ca_2B_6O_{11}\cdot 7H_2O$	Kurnakovite	$Mg_2B_6O_{11}\cdot 13H_2O$
Inyoite	$Ca_2B_6O_{11}\cdot 13H_2O$	Inderite	$Mg_2B_6O_{11}\cdot 15H_2O$

Michael Fleischer

Nordite

V. E. Gerasimovsky: Nordite, a new mineral of the Lovozero tundras. *Compt. Rend, Acad. Sci. U.R.S.S.*, **32,** 496–498 (1942).

Name: "Because of its northern origin."

Chemical Properties: A silicate of sodium, strontium, calcium, and rare earths. Analysis by G. A. Burova gave: SiO_2 45.53, Ti, Cb, Ta None, Fe_2O_3 1.84, Ce_2O_3 8.77 (La etc.)$_2O_3$ 10.48, (Y, etc.)$_2O_3$ 0.95, MnO 6.04, SrO 7.40, CaO 4.46, MgO 2.00, Na_2O 11.70, K_2O 0.08, F None, Cl trace, loss on ignition None; Sum 99.25% (given as 99.27). This corresponds to $2Na_2O \cdot 3RO \cdot 0.7\ R_2O_3 \cdot 8SiO_2$, a metasilicate. Before the blowpipe, easily fused to a blue glass. Borax bead in O.F. is light yellowish-green when hot, pale pink when cold. In R.F. paler green when hot, colorless when cold. Decomposed by HCl, HNO_3 and H_2SO_4.

Crystallographic Properties: Orthorhombic, $a:b:c = 0.730:1:0.527$. The measured crystals are poorly developed and do not give distinct signals. The symmetry was confirmed by Laue photographs of (100) and (010) sections. Nordite occurs as lamellae up to 1 cm. long, 0.5 cm. wide and 0.1 cm. thick. Crystals are rare. The forms noted were {100}, {010}, {110}, {120}, {212} and {101}, of which {100} is dominant.

Physical Properties: Color light brown; streak white: semi-transparent. Cleavage {100} good. Fracture uneven to conchoidal. Brittle. Hardness 5–6. G. (pycnometer) = 3.430.

Optical Properties: Optically biaxial, negative. $\alpha = 1.619$, $\beta = 1.630$–1.640, $\gamma = 1.642$, 2V (Fedorov stage) $2V_{Li}$ 32°, $2V_{Na}$ 31°30′, $2V_{Tl}$ 31°30′. $X = \alpha$, $Y = \beta$, $Z = \gamma$.

Occurrence: Found on the left bank of the upper course of the Chinglusuai River, Lovozero alkaline massif, Kola Peninsula. Occurs in pegmatitic patches in a sodalite syenite. Associated minerals are sodalite (variety hackmanite), ussingite, chinglusuite and lomonosovite (a sodium phosphate-titanium silicate). (This last is apparently a new mineral as yet undescribed M. F.). Lamprophyllite, eudialyte, microcline, nepheline, aegirite, sphalerite, neptunite are subordinate minerals.

M. F.

Metaloparite

V. I. Gerasimovsky: Metaloparite, a new mineral from the Lovozero tundras. *Compt. Rend. Acad. Sci. U.R.S.S.*, **33**, 61–63 (1941).

Chemical Properties: An alteration product of loparite. Analysis made on 3 g. by I. D. Borneman—Starynkevitch gave: SiO_2 1.27, TiO_2 44.01, Cb_2O_5 10.78, Ta_2O_5 0.66, ThO_2+rare earths 34.20, CaO+SrO 5.35, K_2O+Na_2O 0.23, H_2O 3.49, Sum 99.99%. In the alteration, Ti, Cb, Ta, and rare earths have not been affected, CaO+SrO have diminished from 8.4 to 5.35, $NaO+K_2O$ from 8.4 to 0.2 and H_2O has increased from 0.6 to 3.5%. Before the blowpipe infusible, turns to brownish-black. Decomposed by H_2SO_4.

Physical and Optical Properties: Color brownish-yellow, streak greenish-yellow. Luster adamantive. Brittle with no cleavage and uneven fracture. Hardness difficult to determine but about 5. G. (pycnometer) 4.41. In thin section, dark brown with a greenish tinge, also dirty yellow-green. Very fine grained. Shows birefringence under high magnication. n 2.24±.03.

Occurrence: Found in hydrothermally altered loparite urtite and loparite lujavrite rocks of the Lovozero alkaline massif, Kola peninsula. Reported from the eastern slope of Mt. Vavnbed, the northern slope of Mt. Ninchurt, the southern slope of Mt. Stratempakhk, the southwestern slope of Mt. Kuftnyun, associated with nepheline which has been altered nearly completely to sericite and zeolites.

M. F.

Unnamed

S. I. Naboko: On a new fluoric mineral occurring in the sublimates of the volcano Klyuchevsky. *Compt. Rend. Acad. Sci. U.R.S.S.*, **33**, 140–143 (1941).

Chemical Properties: Analysis by V. Nekrassova gave: SiO_2 1.80, Al_2O_3 28.26, Fe_2O_3 2.04, MgO 8.65, CaO 11.15, Na_2O 4.62, K_2O 1.07, H_2O- 1.86, H_2O+ 11.60, F 43.40, Cl 0.81; Sum $115.26-(O=F_2,Cl_2\ 18.35)=96.91\%$. As elements, this gives Al 14.96, Mg 5.22, Ca 7.99, Na 3.43, K 0.89, H_2O- 1.86, H_2O+ 11.60, F 43.40, Cl 0.81. This corresponds to $(Na, K)_5(Ca, Mg)_{12}Al_{16}F_{67}\cdot 22H_2O$. (This does not balance; it might rather be given as—$F_{67}(OH)_{10}\cdot 17H_2O$. M. F.) A simplified formula is $NaCaMgAl_3F_{14}\cdot 4H_2O$. Spectrochemical study shows the presence of Be, Cu, Co, V, Cr, Zr, Ga, Ba, and Sr (amounts not stated). The mineral is decomposed by concentrated HCl, not dissolved by other acids.

Physical and Optical Properties: Color light yellow. Under the microscope, light yellow, transparent, turbid owing to minute inclusions. Isotropic, $n=1.383$. X-ray powder pictures show isometric symmetry.

Occurrence: Occurs as crusts and as a powdery cement in broken blocks of lava near the Bilyukai crater of the Klyuchevsky volcano.

Relationships: Closely related to ralstonite, differing in that Ca predominates over Na.

Discussion: Recalculation of the analysis on the assumption that, as in ralstonite (cf. Pabst, *Am. Mineral.*, **24**, 566 (1939), $Al+Mg=16$ gave $(Ca, Na, K)_{7.72}\ (Al, Mg)_{16}\ F_{48}(OH)_{3.61}13.7H_2O$. This fits the requirements of the pyrochlore group approximately. The (Ca, Na) positions are apparently completely occupied (difference from ralstonite) and the water content is twice as high.

M. F.